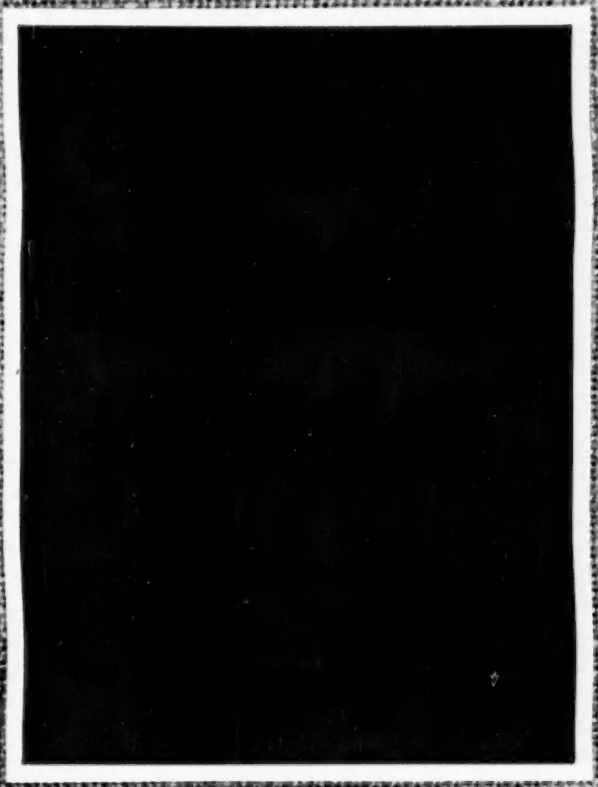

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TEXTILE RESEARCH JOURNAL

# Some Theoretical Considerations of the Dyeing of Cellulose Acetate with Disperse Dyes[1]

**Howard J. White, Jr.**

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**Abstract**

Theoretical aspects of the disperse dyeing of secondary cellulose acetate are considered. Two models for the dyeing process are developed provisionally, one based on mixing of polymer segments with absorbed molecules, one based on absorption onto sites within the fiber. From a consideration of the experimental results available, the model based on mixing is rejected as unsatisfactory. The model based on absorption onto sites is qualitatively consistent with most of the experimental results available. Although both models are crude approximations, the qualitative agreement with experiment shown by the site model offers the possibility that it may be used as a stepping stone to further experiments and development of a more exact theory of disperse dyeing for cellulose acetate.

## Introduction

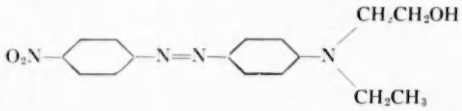
As the use of hydrophobic fibers has increased, the use of disperse dyes and their technological importance have also increased. Gradually a body of information relating to the physical chemistry of disperse dyeing has been built up. Work through 1953 has been discussed by Vickerstaff [29]. There have been many more recent investigations, of which several dealing with the interactions of these dyes with cellulose acetate [1–7, 9–11, 13, 15–19] or polyester fibers [23, 25–28] are cited here.

Although many aspects of the dye–solvent–fiber interaction have been examined, models for further quantitative investigation have been lacking. In general, the dye–fiber interaction is described as some form of solution process akin to liquid–liquid mixing. It is the purpose of this paper to discuss the experimental results available in an effort to provide a more detailed understanding of the mechanism of the absorption process.

Emphasis will be placed on secondary cellulose acetate as a substrate. Although cellulose triacetate and polyester fibers are substrates which are similar to the secondary acetate in some aspects of behavior, each has its own idiosyncrasies and statements based on the behavior of the secondary acetate will, generally, need revision when the other substrates are considered. It is also probable that the disperse dyes should be considered in classes based, perhaps, on capacity to act as electron furnisher or acceptor in hydrogen bonding. Un-

[1] Presented in part during a symposium entitled "Dyeing Behavior of Cellulose and Cellulose Derivatives" sponsored by the Division of Cellulose Chemistry at the Annual Meeting of the American Chemical Society, New York, September 1957.

**TABLE I. Properties of CI Disperse Red I**



| Aq. sol'n, 80° C., mole/l. | Heat of sol'n in water* (kcal./mole) | Melting point, ° C. |
|---|---|---|
| $\sim 23 \times 10^{-6}$ ($\sim$7.5 mg./l.) | 17.5 | 163 |

* From Bird, C. L. and Harris, P. [3].

fortunately, results are not extensive enough to allow a reasonable test for such a classification at the present time, and the dyes will be lumped together in the hope that qualitatively the similarities will outweigh the differences.

## Experimental Results Available

### *The Dyes*

The dyes have the long chains of conjugated double bonds needed to give them color and are generally relatively rigid and flat as a result. In addition they almost always contain hydrogen donating and/or accepting groups which can participate in hydrogen bonding. They are generally of smaller molecular weight than the direct dyes and do not contain ionizable groups.

Bird and coworkers [1, 3] have studied the solubilities of many disperse dyes in water. The solubilities are small ($\sim 10^{-4}$ $M$/l.) and $\sim$16 kcal./$M$ of heat are absorbed in the solution process.

The dyes are crystalline, relatively high melting, and have relatively low vapor pressures [7, 20].

Properties of the azo dye, Disperse Red I, are given in Table I.

### *The Fiber and the Dyed Fiber*

Secondary cellulose acetate contains hydroxyl and acetate groups in about the ratio 1:5. Fibers of secondary acetate possess a low degree of crystallinity and are oriented to some extent. Appropriately dyed fibers are dichroic [21, 22], showing that the dye molecules are oriented along the (oriented) polymer chains.

Second-order transitions in secondary acetate have been studied by Brown [8] (fibrous samples) and Russell and van Kerpel [24] (bulk samples). Both sets of workers, using stiffness as a measure of change, found a large decrease about 150° C. Russell and van Kerpel measured changes in specific volume and found transitions at 55° C. and 110° C. As might be expected, plasticizers caused a decrease in the transition temperatures. The two sets of measurements suggest that some unfreezing of motions (possibly involving acetate groups) occurs at lower temperatures but the large-scale motions of chain segments which might result in marked changes in mechanical properties do not occur below 150° C. Conventional dyeing takes place below 100° C and, although minor changes in fiber properties may result from dyeing, major changes could not be tolerated and do not, in fact, occur.

Secondary acetate absorbs a considerable amount of water, $\sim$20% by weight from liquid water at room temperature by the centrifuge method [13]. The results of Wiegerink [30] show that the absorption of water is exothermic, at least at lower relative humidities. It seems probable that the uptake at the highest relative humidities is not very sensitive to temperature. In any event the fiber contains an appreciable amount of water during the dyeing process.

### *The Dyeing Process*

Early work [29] indicated that, although most of the dye was present in the dyebath in particulate form, it was the molecularly dispersed dye that was responsible for dyeing. Experiments with true solutions in water have shown that the amount absorbed is a linear function of the concentration of dye in true solution in the bath up to saturation. These linear isotherms have been found for a variety of dyes and represent one of the most unique features of disperse dyeing from aqueous solution.

Since the absorption isotherm is linear, the proportionality constant provides a measure of the standard partial molal free energy change on transferring dye from solution at unit activity to fiber at unit activity. The change of the proportionality constant with temperature shows that heat is given off when dye is transferred from solution to the

fiber [3]. Thus the concentration of dye in solution required to produce a given absorption rises with temperature. The activity of dye in solution is probably proportional to the molality, since the dye is not very soluble in water. In general, the water content of the fiber can change with temperature along with the dye content, and the state of unit dye activity within the fiber may (and probably does) refer to different compositions of the fiber phase. As a result the process for which the change in the proportionality constant with temperature defines a heat is obscure. The amount of dye absorbed from a saturated solution usually increases with increasing temperature, the increase in solubility overcoming the effects of the exothermic transfer process [3, 18, 20, 23]. Azobenzene, which is used, on occasion, as a model compound, is an exception [20]. Isotherms for Disperse Red I are shown in Figure 1.

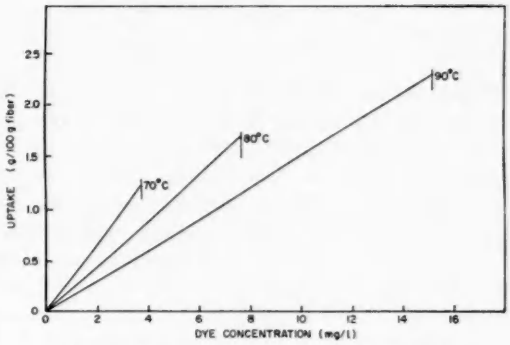



**Fig. 1.** Absorption isotherms for CI Disperse Red I from water [3].

Absorption measurements from solvents other than water [15] have shown that nonlinear isotherms may be obtained (Figure 2). The plot of the amount of dye absorbed against the fraction of saturation of dye in the dyebath for the various solvents shows that each solvent produces its own characteristic curve. The amount of dye absorbed at a given fraction of saturation from a hydrophobic solvent such as benzene is greater than the amount from a hydrophilic solvent such as methanol. The dye used, Disperse Red I, was only slightly soluble in the solvents selected so that the activity of the dye should be proportional to its concentration in the solution. Under these conditions, a given fraction of saturation refers to the same partial molal free energy of dye in every solvent. The fact that different curves were obtained for the different solvents indicates that the solvents used were directly influencing the dye–fiber interaction and not merely acting as inert transfer agents. (The term "inert" here refers specifically to the influence of the solvent on the dye–fiber interaction and not to any dye-solvent interaction in solution, which has already been taken into account.) There is a qualitative inverse relationship between amount of dye absorbed at a given fraction of saturation and the capacity of the solvent to swell the fiber, so that the results cannot be accounted for by changes in accessibility resulting from swelling.

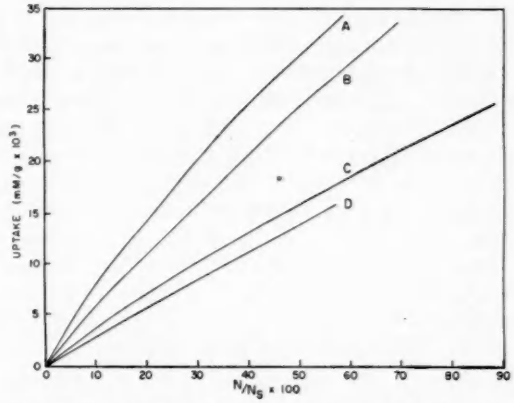



**Fig. 2.** Absorption isotherms for CI Disperse Red I from various solvents at 25° C. [15]. A, benzene; B, $CCl_4$; C, methanol; D, butyl acetate.

Isotherms for absorption from the vapor phase of five dye prototypes have been measured in the temperature range 120° C.–160° C. [20]. Heats of absorption from the vapor phase and of condensation to the crystal were obtained. The isotherms for vapor absorption were linear or slightly concave to the pressure axis. The heats of condensation to the crystal were more exothermic than the heats of condensation to the fiber. The heats of association with the fiber obtained by combining the heats of condensation to the crystal, solution, and dyeing (as measured from the temperature coefficient of the partition coefficient) were the same as, or slightly more exothermic than, the heats of condensation to the fiber. Thus the fiber did not contain sites for absorption of higher energy than those offered by the crystal. The dye prototypes used were azobenzene, *p*-nitroaniline, N,N′-dimethyl-*p*-nitroaniline, *p*-aminoazobenzene, and N,N′-dimethyl-*p*-aminoazobenzene. Heats associated with the absorption of N,N′-dimethyl-*p*-aminoazobenzene are shown in Figure 3.

## Theoretical Considerations

*Disperse Dyeing as Dissolution in the Fiber*

Cellulose acetate shows no evidence of having large pores; it is soluble in several organic solvents which also dissolve appreciable quantities of many disperse dyes; it is thermoplastic. There is no evidence for sites of high bonding energy for the dye (at least, as compared to the dye crystal), and the absorption isotherms for the dyes are linear from aqueous solution. For the above reasons the partitioning of dye between water and the fiber is often considered to be analogous to the partitioning of a solute between two simple immiscible organic liquids, in which case a linear isotherm for partitioning is also obtained.

To consider the validity of the analogy further, it is convenient to examine the properties of simple solutions. It is fundamental to the concept of a simple solution that any molecule in the solution be capable of occupying any unit of volume within the solution with equal probability. This equal probability of occupancy leads directly to the well-known dependence of the partial molal free energy of the solute on its mole fraction in the solution. In the simplest cases there is no other concentration-dependent term in the partial molal free energy. Thus, the linear isotherm for partitioning between two simple immiscible solvents is a direct result of the similarity of form of the partial molal free energy of the solute in each of the two solutions. For more complex solutions, deviations are observed, although all partitioning isotherms must become linear for sufficient dilution.

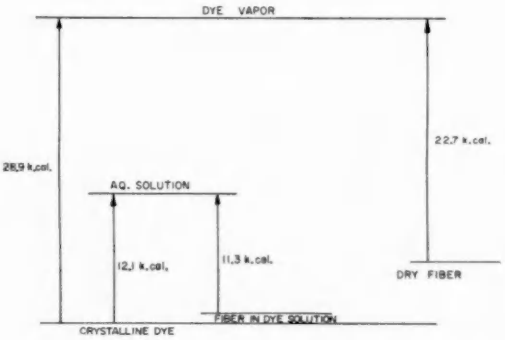
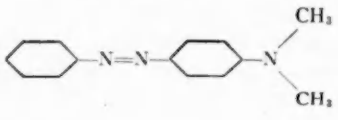



**Fig. 3.** Heats associated with the absorption of




[18, 20].

For polymer solutions, deviations from simple behavior are observed at unusually low concentrations because the residues in the polymer chains are constrained to adjoin one another at all times; in a swollen cross-linked gel even further constraints exist because of the junction points. Flory [12] has examined the thermodynamic properties of such gels in detail. If it is assumed that both solvent and solute in the external solution (water and dye) are dissolved in the fiber, a simple extension of Flory's development to two solutes gives

$$\ln N/N_S = \ln v_3 + \left(1 - \frac{1}{x}\right) v_2 - X_{12} v_1 v_2 + X_{23} v_2 (1 - v_3) + X_{13} v_1 (1 - v_3) + \frac{\nu V_3}{V_2}\left(v_2^{\frac{1}{3}} - \frac{v_2}{2}\right) \quad (1)$$

where $N$ and $N_S$ are the mole fraction of dye in the solution and in a saturated solution; $v_1$, $v_2$, $v_3$ are the volume fractions of water, polymer, and dye respectively in the polymer phase; $x$ is the number of mobile units between cross links; $\nu$ is the effective number of chains in the network; $V_2$ the dry volume of the polymer, $V_3$ the molar volume of the dye, and the $X_{ij}$ are measures of the heats of interaction.

$$X_{12} = \frac{z \Delta w_{12}}{kT}$$

where

$$\Delta w_{12} = w_{12} - \tfrac{1}{2}(w_{11} - w_{22})$$

where $z$ is the coordination number and $w_{ij}$ is the energy associated with an $ij$ pair contact. The first two terms on the right hand side of Equation 1 arise from the mixing of the dye, solvent, and polymer molecules, the next three from interaction energies, and the last from the potential energy of the stretched polymer network.

If $v_3$ is sufficiently small, $v_2$ and $v_1$ become effectively constant and $|\ln v_3| \gg v_3$. In this case $v_3$ is proportional to $N$ and a linear isotherm results. (Since the dyes are not very soluble, $N$ is proportional to $C$.) It is difficult to estimate the shape of the dependence represented by Equation 1 without numerical values for the constants. However, $v_3$ is probably nearly a linear function of $N$ up to $v_3 \cong 0.01$, because the dye solution is so dilute that the activity of the solvent, hence (probably) the solvent content of the polymer phase, are only

slightly dependent on dye concentration. The uptake of dye from a saturated solution ranges from 1% to 10% at 80° C. [3], with higher values to be expected at higher temperatures. Thus Equation 1 could provide a linear isotherm over at least part of the range of uptakes, which is important. However, the difficulties with Equation 1 do not arise from its shape alone. The equation was not intended to apply to such a concentrated gel of stiff chains as is present in water-swollen cellulose acetate. An equation designed to apply to such a gel would have additional (or different) terms. However, it is clear that deviation from a linear relationship would occur at even lower uptakes than with Equation 1, since this equation, representing the behavior of a slightly cross-linked, randomly organized net of flexible chains, gives an upper limit for the mixing of real molecules with real networks. (Although cellulose acetate is not cross-linked, the highly organized regions presumably hold it together and act as cross links in solvents such as water which possess limited swelling power.)

In addition to the above argument, which is essentially quantitative in nature, there are other difficulties preventing acceptance of the entropy of mixing as the primary source of dye absorption. None of the properties of cellulose acetate fibers are suggestive of extensive mobility of chains in the region in which dyeing usually occurs (<100° C.) and dichroism of dyed samples is indicative of oriented absorption.

*Disperse Dyeing as Absorption onto Sites*

*Derivation of isotherm.* Since there is no direct evidence against absorption onto sites, it would seem worthwhile to examine the possibilities of explaining the phenomena of disperse dyeing in this way. Since competition for absorption sites with hydrogen-bonding solvents has previously been postulated [15] to account for the effect of solvent type on dyeing, it presumably should be taken into account. To provide a simple model for quantitative development, it will be assumed:

that there exists one type of absorption site for the dye within cellulose acetate;
that solvent is absorbed on the same sites as the dye;
that there is no multilayer formation on the sites involved in dye absorption, when they are covered with either dye or solvent, and no interactions between absorbed molecules are important;
that there are no appreciable contributions to the free energy of absorption from swelling of the polymer network or mixing;
that the aqueous dye solution can be considered to be an ideally dilute solution.

The partition function for an absorbed dye molecule can be written

$$q_D = j_D \left( \frac{kT}{h\nu_D^A} \right)^3 e^{\epsilon_D^A/kT} \tag{2}$$

where $\epsilon_D^A$ is the potential energy needed to remove an absorbed molecule into a vacuum, $j_D$ includes all internal degrees of freedom, including states involving torsional vibration of the molecule as a whole in its absorbed states, and $\nu_D^A$ is an average frequency of translational vibration of the molecule in its absorbed state.

The partition function for an absorbed solvent molecule can be written

$$q_S = j_S \left( \frac{kT}{h\nu_S^A} \right)^3 e^{\epsilon_S^A/kT} \tag{3}$$

where $j_S$, $\epsilon_S^A$, and $\nu_S^A$ have meanings analogous to those for the dye.

The partition function for the polymer plus absorbed molecules can be written

$$Q = \frac{B!}{n_S!\, n_D!(B - n_S - n_D)!} j_D{}^{n_D} j_S{}^{n_S} \times \left( \frac{kT}{h\nu_D^A} \right)^{3n_D} \left( \frac{kT}{h\nu_S^A} \right)^{3n_S} e^{n_D\epsilon_D^A/kT}\, e^{n_S\epsilon_S^A/kT} q_p \tag{4}$$

where $B$ is the number of sites available for absorption, $n_S$ and $n_D$ are numbers of molecules of solvent and dye absorbed, and $q_p$ is the partition function for the pure polymer.

The partial molal free energies of the dye and solvent can be obtained from $Q$ (neglecting a small $PV$ term) and written

$$\mu_D = \mu_{OD}^A + kT \ln \frac{\theta_D}{1 - \theta_D - \theta_S} \tag{5}$$

and

$$\mu_S = \mu_{OS}^A + kT \ln \frac{\theta_S}{1 - \theta_S - \theta_D} \tag{6}$$

where

$$\theta_D = \frac{n_D}{B}, \quad \theta_S = \frac{n_S}{B},$$

and

$$\mu_{OD}^{A} = -kT \ln j_D - \epsilon_D^A - kT \ln \left( \frac{kT}{h\nu_D^A} \right)^3 \quad (7)$$

and

$$\mu_{OS}^{A} = -kT \ln j_S - \epsilon_S^D - kT \ln \left( \frac{kT}{h\nu_S^A} \right)^3 \quad (8)$$

The partial molal free energies of the dye and the solvent in the solution can be written

$$\mu_D = \mu_{OD}^{O} + kT \ln N/N_{Sat} \quad (9)$$

$$\mu_S = \mu_{OS}^{O} + kT \ln (1 - N) \quad (10)$$

where $N$ is the mole fraction of dye in the solution, $N_{Sat}$ the mole fraction at saturation, $u_{OS}^{O}$ the molal free energy of the pure solvent under the same conditions of temperature and pressure, and $u_{OD}^{O}$ the molal free energy of the crystalline dye.

If $k_S$ and $k_D$ are defined by the equations

$$k_S \equiv e^{(\mu_{OS}^{O} - \mu_{OS}^{A})/kT} \quad (11)$$

$$k_D \equiv e^{(\mu_{OD}^{O} - \mu_{OD}^{A})/kT} \quad (12)$$

the following isotherms can be written, on using the conditions of equilibrium

$$\theta_D = \frac{N/N_{Sat}}{\frac{1}{k_D} + \frac{k_S}{k_D} + N/N_{Sat}\left(1 - \frac{k_S}{k_D} N_{Sat}\right)} \quad (13)$$

and

$$\theta_S = \frac{\frac{k_S}{k_D}\left(1 - N_{Sat}\frac{N}{N_{Sat}}\right)}{\frac{1}{k_D} + \frac{k_S}{k_D} + \frac{N}{N_{Sat}}\left(1 - \frac{k_S}{k_D} N_{Sat}\right)} \quad (14)$$

To investigate the behavior of Equation 13, consider various values of $\frac{k_S}{k_D}$:

i) $\frac{k_S}{k_D} = 0$; solvent is not absorbed

$$\theta_D = \frac{N/N_{Sat}}{1/k_D + N/N_{Sat}} \quad (15)$$

which is Langmuir's isotherm.

ii) $\frac{k_S}{k_D} = \frac{0.1}{N_{Sat}}$

$$\theta_D = \frac{N/N_{Sat}}{\frac{1}{k_D} + \frac{k_S}{k_D} + 0.9\frac{N}{N_{Sat}}} \quad (16)$$

iii) $\frac{k_S}{k_D} = \frac{1}{N_{Sat}}$

$$\theta_D = \frac{N/N_{Sat}}{\frac{1}{k_D} + \frac{k_S}{k_D}} \quad (17)$$

which is a linear isotherm.

iv) $\frac{k_S}{k_D} \gg \frac{1}{N_{Sat}}$

$$\theta_D = \frac{N/N_{Sat}}{\frac{1}{k_D} + \frac{k_S}{k_D} - \frac{N}{N_{Sat}}\left(\frac{k_S}{k_D} N_{Sat} - 1\right)} \cong \frac{N/N_{Sat}}{\frac{1}{k_D} + \frac{k_S}{k_D}} \quad (18)$$

which is linear or slightly convex to the $N/N_{Sat}$ axis.

Thus the isotherm can be a Langmuir isotherm or essentially linear depending on the value of $k_S/k_D$ as long as $N_{Sat} \ll 1$. Examples for various values of $k_S/k_D$ and $k_D$ with $N_{Sat} = 0.01$ are given in Figures 4 and 5. The isotherms are quite linear for $k_S/k_D > 1$, especially when $k_D$ is small.

*Effects of temperature.* To proceed further, in particular to evaluate the effect of temperature on the absorption isotherm, it is necessary to evaluate the constants $k_S$ and $k_D$ and to consider the behavior of $N_{Sat}$. It will be assumed that the solid dye can be approximated by an Einstein crystal, that the harmonic oscillator model is adequate for the liquid solvent and the dye solution, and that the dye solution is an ideal dilute solution (see Fowler and Guggenheim [14] for a discussion of the nature of these approximations). These are drastic assumptions, but should be adequate since the interest here is more in the form of functional dependence than in the evaluation of the magnitudes of various effects.

Assuming $kT \gg h\nu$

$$u_{OD}^{O} \cong -\epsilon_D^O - 3kT \ln \frac{kT}{h\nu_D^O} - kT \ln j_D^O \quad (19)$$

where $\epsilon_D^O$ is the energy required to transfer a molecule of dye from the crystal to vacuum, $\nu_D^O$ is an average frequency of vibration for the three modes of vibration of the molecule as a whole about its equilibrium position in the crystal, and $j_D^O$ is an "internal" partition function including terms for torsional vibration about equilibrium positions in the crystal.

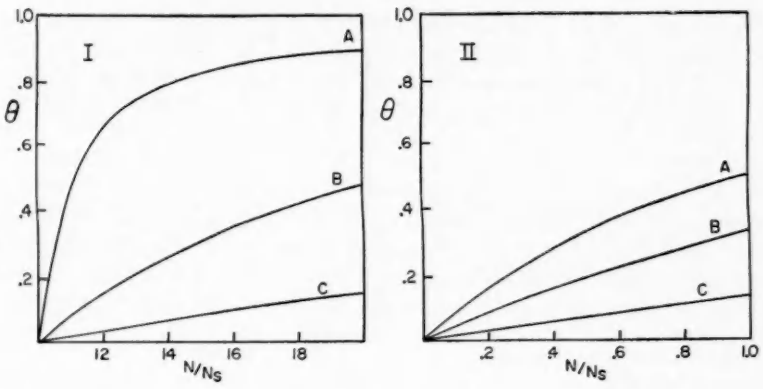



**Fig. 4.** Theoretical absorption isotherms.
I) $k_D = 10$ II) $k_D = 1$
A) $\frac{k_S}{k_D} = 0$ B) $\frac{k_S}{k_D} = 1$ C) $\frac{k_S}{k_D} = 5$

By use of the harmonic oscillator model for the solvent

$$u_{OS}^{O} = -\epsilon_S - 3kT \ln \frac{kT}{h\nu_S^O} - kT - kT \ln j_S^O \quad (20)$$

where $\epsilon_S^O$, $\nu_S^O$, and $j_S^O$ have meanings analogous to those of similar terms in Equation 19.

Equations 19, 12, and 7 can be combined to give

$$\ln k_D = \frac{-\epsilon_D^O}{kT} + \frac{\epsilon_D^A}{kT} - 3 \ln \frac{h\nu_D^A}{h\nu_D^O} - \ln \frac{j_D^O}{j_D^A} \quad (21)$$

and Equations 20, 11, and 8 give

$$\ln k_S = -\frac{\epsilon_S^O}{kT} + \frac{\epsilon_S^A}{kT} - 1 - 3 \ln \frac{h\nu_S^A}{h\nu_S^O} - \ln \frac{j_S^O}{j_S^A} \quad (22)$$

Assuming that $j_D^O = j_D^A$, $j_S^O = j_S^A$, and $\nu_D^O = \nu_D^A$, Equations 21 and 22 can be simplified to give

$$k_D = e^{-(\epsilon_D^O - \epsilon_D^A)/kT} \quad (23)$$

and

$$k_S = \frac{1}{e} \left( \frac{\nu_S^O}{\nu_S^A} \right)^3 e^{-(\epsilon_S^O - \epsilon_S^A)/kT} \quad (24)$$

Using

$$u_D = -\epsilon_D^O + w_{DS} - kT \ln (\phi_D v_D) - kT + kT \ln N \quad (25)$$

where $w_{DS}$ represents the excess energy of interaction between dye and solvent and $\phi_D$ and $v_D$ are essentially internal terms,

$$N_{Sat} = \left( \frac{h\nu_D^O}{kT} \right)^3 e e^{-w_{DS}/kT} \frac{1}{j_D^O} \phi_D v_D \quad (26)$$

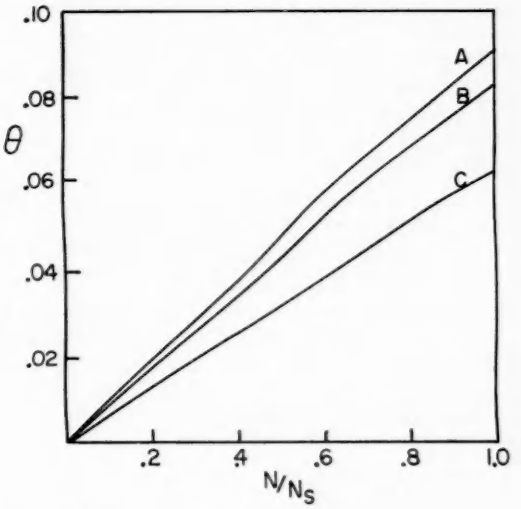



**Fig. 5.** Theoretical absorption isotherms.
$k_D = 0.1$
A) $\frac{k_S}{k_D} = 0$ B) $\frac{k_S}{k_D} = 1$ C) $\frac{k_S}{k_D} = 5$

This can be reduced, using a harmonic oscillator model for the solution, to give

$$N_{Sat} = \left( \frac{\nu_D^O}{\nu_D^{Soln}} \right)^3 e e^{-w_{DS}/kT} \quad (27)$$

The easiest temperature effect to consider is that on the uptake of dye from a saturated solution, which can be expressed by differentiation of Equation 13 as

$$\left( \frac{\partial \theta_D}{\partial T} \right)_{N/N_{Sat}=1}$$

$$= \frac{-\frac{1}{k_D^2}\frac{\partial k_D}{\partial T} + (1 - N_{Sat})\frac{\partial \frac{k_S}{k_D}}{\partial T} - \frac{k_S}{k_D}\frac{\partial N_{Sat}}{\partial T}}{\left(\frac{1}{k_D} + \frac{k_S}{k_D}(1 - N_{Sat}) + 1\right)^2} \quad (28)$$

Using

$$\frac{\partial k_D}{\partial T} = k_D \frac{\epsilon_D^O - \epsilon_D^A}{kT} \quad (29)$$

$$\frac{\partial \frac{k_S}{k_D}}{\partial T} = \frac{k_S}{k_D}\frac{(\epsilon_S^O - \epsilon_S^A - \epsilon_D^O + \epsilon_D^A)}{kT^2} + 3\frac{k_S}{k_D}\left(\frac{\nu_S^A}{\nu_S^O}\right)\frac{\partial\left(\frac{\nu_S^O}{\nu_S^A}\right)}{\partial T} \cong \frac{k_S}{k_D}\frac{(\epsilon_S^O - \epsilon_S^A - \epsilon_D^O + \epsilon_D^A)}{kT^2} \quad (30)$$

$$\frac{\partial N_{Sat}}{\partial T} = N_{Sat}\frac{w_{DS}}{kT^2} + 3\,N_{Sat}\left(\frac{\nu_D^{Soln}}{\nu_D^O}\right)\frac{\partial\left(\frac{\nu_D^O}{\nu_D^{Soln}}\right)}{\partial T} \cong N_{Sat}\frac{w_{DS}}{kT^2} \quad (31)$$

then

$$\left(\frac{\partial \theta_D}{\partial T}\right)_{N/N_{Sat}=1} = \left[\frac{1}{k_D}\frac{(\epsilon_D^O - \epsilon_D^A)}{kT^2} - (1 - N_{Sat}) \times \frac{k_S}{k_D}\frac{(\epsilon_S^O - \epsilon_S^A - \epsilon_D^O - \epsilon_D^A)}{kT^2} + \frac{k_S}{k_D}N_{Sat}\frac{w_{DS}}{kT^2}\right] \div \left(\frac{1}{k_D} + \frac{k_S}{k_D}(1 - N_{Sat}) + 1\right)^2 \quad (32)$$

If it is assumed that $\epsilon_D^O > \epsilon_D^A$ (as is made plausible by Majury's work [20]), there are two cases:

i) $\epsilon_S^O < \epsilon_S^A$. The solvent is strongly absorbed and $\theta_D$ increases with $T$ since very term in the numerator is positive.

ii) $\epsilon_S^O > \epsilon_S^A$. The center term in the numerator can become negative; however, $k_S$ becomes small so that it seems likely that the first term will become dominant and $\theta_D$ will still increase with $T$.

Thus the results are consistent with experimental results.

Another more common temperature coefficient is $(\partial N/\partial T)_\theta$. An expression can be derived for this coefficient, but, since it contains both positive and negative terms, it is not possible to say in general terms whether $N$ increases or decreases with $T$ for a given value of $\theta$. The results depend on the solubility properties of the dye as well as on the dye–fiber interaction.

A third temperature coefficient is also worth mentioning. Since the experimental isotherms are linear, a heat can be obtained from the temperature dependence of the slope. In essence $\frac{\partial(R \ln \theta/N)}{\partial \frac{1}{T}}$ is evaluated. If Equation 18 is accepted as a proper expression for the linear isotherm, then the heat can be evaluated to give

$$-\Delta H_D{}^O = \frac{\partial(R \ln \theta/N)}{\partial \frac{1}{T}} = -(\epsilon_D{}^O - \epsilon_D{}^A) + w_{DS} + \frac{k_S}{1 + k_S}(\epsilon_S{}^O - \epsilon_S{}^A) \quad (33)$$

However $w_{DS}$ is the heat of solution and can also be evaluated experimentally. Bird and Harris [3] have tabulated $\Delta H_D^O$ and $w_{DS}$ for a number of dyes. On the average $-\Delta H_D^O - w_{DS} = -5$ kcal./mole, which is in agreement with the expected sign for the remaining two terms in Equation 33. Thus the theory is consistent with the experimental results.

*Influence of solvent type.* The effects of change of solvent as shown in Figure 2 can be explained reasonably. Solvents capable of hydrogen bonding compete with the dye for absorption sites and result in linear, or at least flatter, isotherms. Solvents which do not form hydrogen bonds result in greater uptake at a given $N/N_{Sat}$ and give more curved isotherms.

It should be mentioned that a certain amount of penetration of the fiber by the solvent is necessary if the dyeing is to proceed at a reasonable speed. Whether this is exclusively a kinetic effect or if other factors, such as a change in accessibility of sites within the fiber, are important remains to be seen. A change in accessibility could result in an effective change in the number of sites available for absorption.

*Heat relationships.* The results of Majury [18, 20] on the various heat terms relevant to the dyeing process (as for example, those in Figure 3) are not

in complete agreement with the theory. By use of Equation 33, the heat of transfer of dye from the crystal to the fiber via solution can be written

$$\Delta H = \epsilon_D^G - \epsilon_D^A + \frac{k_S}{1 + k_S} (\epsilon_S^A - \epsilon_S^G) \qquad (34)$$

while the heat of transfer via the vapor is

$$\Delta H_v = \epsilon_D^G - \epsilon_D^A \qquad (35)$$

In other words, the heat absorbed in going from the crystal to the dyed fiber is greater via solution than via vapor according to the theory, whereas experimentally the reverse is apparently true. Two possible reasons for the discrepancy can be advanced. First, a dye molecule absorbed from the vapor phase must swell the fiber to make room for itself; however, when dyeing from solution occurs, the fiber is already partly swollen by the solvent. It may be that the work of expanding the fiber to permit dye absorption, which is not taken into account in the theory, is different in the two cases, with the work of swelling (per dye molecule absorbed) greater from the vapor phase. Second, lateral interactions between absorbed molecules have been ignored. Comparison of the heats of vaporization and of solution of the dye show that, although the dye is not very soluble in water, there is still appreciable interaction between the dye and water. It may be that interaction with adjacent water molecules (not even necessarily absorbed on sites in competition with dye) is enough to cause the difference.

## Discussion

Equations have been developed for models of the dyeing process involving simple mixing and absorption onto sites. The model involving mixing was rejected as probably unsatisfactory quantitatively and presenting an unrealistic picture of the internal behavior of cellulose acetate fibers. The model involving absorption onto sites is capable of supplying the linear isotherm from aqueous solution observed experimentally and is consistent with what results exist on the effect of temperature on the isotherm and the effects of change of solvent. What differences exist on comparison with results on absorption from the vapor phase can probably be attributed to effects not explicitly considered in the simple theory. The theory does not seem to be at variance with what is known of the structural properties of cellulose acetate.

The theory has been put forth for secondary cellulose acetate. It might be argued that linear isotherms are found with polyester fibers and triacetate fibers, neither of which absorb appreciable amounts of water. For such fibers, competition for hydrogen-bonding sites is less appealing. Two remarks may be made in this connection. First, the amounts of dye absorbed represent a few percent on the weight of the fiber. Since the dyes have molecular weights of several hundred g./$M$, an equivalent amount of water represents a few tenths of a percent on the weight of the fiber. All but the most hydrophobic fibers absorb at least that amount from liquid water. Second, Figures 4 and 5 show that, if $k_D$ is small, the isotherms are essentially linear even if $k_S = 0$.

Some question might be raised about the ability of disperse dyes and polymers containing ester groups to form hydrogen bonds, especially in the presence of solvents such as water. The work of Giles and coworkers [9–11] seems to indicate that they can.

It should not be inferred that hydrogen bonding is the only possible mode of attachment of the dye to the fiber. The rigid flat structure of the dye molecules enables them to fit closely to appropriate solid surfaces with a minimum loss of entropy and a maximum amount of bonding by dispersion forces and by dipole interaction. So far the effects of hydrogen bonding seem to be important. If further experimental results should show a class of dyes characterized by small values of $k_D$, it might be that an approach such as is used for mobile monolayers would prove fruitful. In this case the dyes would not be considered to be absorbed onto sites but rather to be held by potential fields near internal surfaces in the fiber with the possibility of relatively free lateral motion along the surfaces. In such a case the influence of the solvent would presumably result from alteration of the potential fields associated with the internal surfaces. Such speculations must remain unresolved until more experimental results are available; however, normally the behavior of molecules absorbed in a mobile monolayer would resemble that of molecules on sites.

## Acknowledgment

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# Changes in Fine Structure and Mechanical Properties Induced by Cyanoethylation of Cotton Yarns

## Part I: Treated Without Tension[1]

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**Abstract**

Cotton yarns were impregnated with 6% sodium hydroxide and reacted in the relaxed state with acrylonitrile at 60° C. and different periods of time up to 60 min. to give products with degrees of substitution up to 2.6 cyanoethyl groups per anhydroglucose unit. As substitution increases, the x-ray diffraction pattern shows only slight alteration until substitution has exceeded 1.1, after which the crystalline structure rapidly gives way to an amorphous structure, complete at about DS = 2.0. At the same time density decreases nearly linearly with substitution. At the stage where the product becomes essentially amorphous, it can be annealed at temperatures of about 175° C. into a new pattern characteristic of cyanoethyl cellulose. This annealing is accompanied by a substantial density increase. Stress relaxation of the cyanoethylated yarns at a substitution of 1.1 suggests a glass–rubber transition point about 140° C. which becomes more distinct and moves to lower temperatures as substitution increases. At a substitution of about 2.0 the stress relaxation reaches its lowest value (about 4% of the value at 20° C.) at the highest temperatures tested (220° C.). With further substitution a minimum relaxation at an intermediate temperature is followed by increasing stress as the temperature is raised. This effect is associated with crystallization. Breaking strength increases slightly at low substitutions but decreases then to less than 50% for the highest substitutions. Elongation at break increases gradually, exceeding 100% above the control at DS = 2 and above. Tensile stiffness decreases to about 3% of its initial value. Work of rupture and recovery show considerable decreases below DS = 2, but sharp rises between 2.0 and 2.6. Immediate elastic recovery is little affected below DS = 2, but rises above this. Delayed elastic recovery shows continuous improvement as substitution increases, eventually exceeding the control by nearly 50%.

### Introduction

Although the mechanical properties of partially cyanoethylated cotton have been discussed in previous communications [4, 5], it was felt that more complete information was needed to fill in some of the gaps. Accordingly, studies were undertaken to prepare cyanoethylated yarns at a wide range of substitutions under suitable conditions in order to determine the basic mechanical properties [12] of cyanoethylated cotton. It was decided to conduct such studies on yarns reacted both in the relaxed state and when held to fixed length. The present paper reports on the first of these objectives.

### Experimental Methods

*Samples*

The yarn used in the present study was spun 14:Z11/2:S8 (42 × 2 tex) from Deltapine cotton with 3.00 twist multiplier (TM) in both singles and ply.

In preparation for reaction with acrylonitrile, samples and their appropriate controls weighing 8–9 g. were immersed in 450 ml. of 6% sodium hydroxide, containing 0.1% Alkamerse [3] wetting agent, subjected to vacuum for a few minutes to remove air bubbles, and then allowed to stand in the alkali. In order to secure maximum reaction, one pair was

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] Use of a company and/or product name by the Department does not imply approval or recommendation to the exclusion of others which may also be suitable.

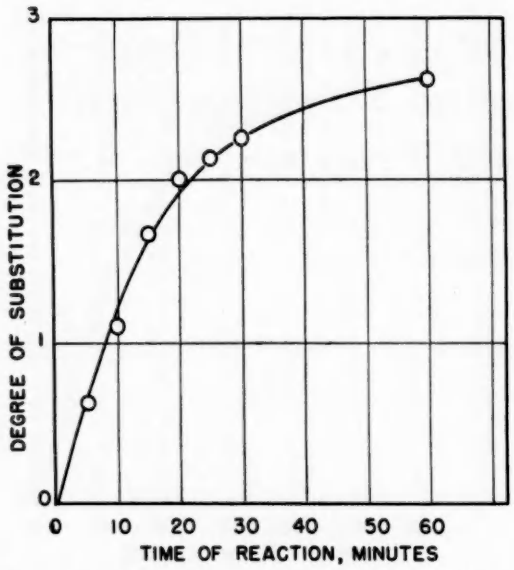


**Fig. 1.** Relation of degree of cyanoethylation to time of reaction.

immersed in 450 ml. of an 8% solution of sodium hydroxide, containing 90 g. of 2,4-dimethylbenzene sulfonic acid sodium salt.

After standing 30 min. at room temperature, the skeins were centrifuged to a wet pickup of 90–100% and reacted with 475 ml. of acrylonitrile, preheated to 60° C. Reaction was allowed to proceed at this temperature for 5–60 min., selected to give substitutions from 0.62 to 2.62.

Control samples were heated for the same periods, using toluene, with which no reaction occurred, in place of acrylonitrile. Additional controls were prepared with 6% sodium hydroxide only.

At the completion of the reaction, the skeins were immersed in 5% acetic acid to neutralize residual alkali, washed with water, then with ethanol and ether, and finally air dried. The degrees of substitution thus obtained, plotted against reaction time, are presented in Figure 1.

It will be noted that the substitution achieved can be represented by a smooth curve.

*Methods*

The degree of substitution was computed from the nitrogen content, determined by the Kjeldahl method.

Yarn shrinkage resulting from the treatment was determined on approximately 36-in. lengths of the yarn in loops, tied before the treatment several feet away from a free end of the skein and measured before and after treatment under low tension. The tension $T$, in grams, was chosen on the basis of the equation

$$T = 156/N \ (= 22 \text{ g. for } 14/2)$$

where $N$ is the cotton yarn number (ASTM D204-57T) [1].

Density was determined on small portions of the reacted samples by the method of Orr and others [10], using calibrated glass beads at close density intervals, and xylene–carbon tetrachloride as the media. The samples were thoroughly dried in a desiccator and then boiled 15–20 min. in carbon tetrachloride before introduction into the density gradient tube.

X-ray tracings were recorded with a Philips Electronics Inc. high precision Diffractometer [3] using a copper target and a potentiometer recorder. Reacted yarn was cut to pass a 20-mesh screen, pressed into a thin plate, and the diffraction detected with a Geiger tube. In some cases thin plates were heated for 30-min. intervals at successively higher temperatures and the diffracted intensity at the position ($2\theta = 10.3°$) of the interference of cyanoethylated cellulose traced.

For quantitative measurements of the intensity, the area under the x-ray diffractometer curve was first measured with a planimeter between the angular $2\theta$ limits of 5° and 30° and the heights of the curves adjusted for a common area. The 002 peak of cellulose at $2\theta = 22.6°$ was then adjusted to the initial cellulose content (to correct for dilution with cyanoethyl groups). The background at $2\theta = 10.3°$, corresponding to the interference of cyanoethylcellulose, was adjusted for dilution by cyanoethyl groups.

Attempts to determine crystallinity by means of the infrared index of crystallinity [9] were not successful, since measurements of intensity at 6.98$\mu$ could not be made. An interferring band at 7.1$\mu$ arises, apparently, from some mode associated with the methylene groups of the cyanoethyl moiety.

Stress relaxation was determined with the aid of a TRI Schaevitz [3] instrument, modified by incorporation of a variable temperature oven around the specimen according to a procedure described by Brown [1]. The 5-in. long specimen was stressed twice to extension corresponding to about 10% of the breaking load and relaxed. The average stress developed during the two loadings was recorded.

The temperature was raised rapidly (10–20 min.) about 20° C. and the two extensions repeated. This process was repeated from room temperature to about 220° C. in 10–20° C. intervals. In some cases the stress was determined at decreasing temperature intervals, by allowing the samples to cool. Small deviations of stress of samples were adjusted to a common initial stress of 120 g.

Bundle breaking strength was determined on six bundles, each containing six strands of yarn fixed in the Pressley jaws and broken on the Instron [3] tester using $\frac{1}{8}$-in. specimen lengths. Increases in weight due to chemical substitution were allowed for in expressing the results of these and yarn tensile tests using breaking strength rather than tenacity since the cyanoethyl group does not become a tensile component of the long cellulose chain backbone. Results were expressed in terms of the mean tex of the controls.

Breaking strength and ultimate elongation of the yarns were determined on five replicate yarns on an Instron [3] tester using a 10-in. specimen length and cross-head speed corresponding to 100% elongation per minute.

Tensile stiffness was determined by division of the breaking strength by the fractional elongation of the yarns at break.

Yarn number was determined from the weights of the specimens from the load–elongation measurements, which were cut between the jaws.

Energy required for rupture was determined with a planimeter from the area beneath the stress–strain curves of ruptured yarns.

Elastic recovery of the yarns from 6% extensions was determined in triplicate on the second of two consecutive loadings made with an Instron [3] tester and the results analyzed as outlined by Susich and Backer [13] into immediate elastic recovery, delayed elastic recovery, and permanent set.

Work recovery of the yarns at 6% or 10% extensions was determined in triplicate with a planimeter from the areas beneath the second of two complete tensile relaxation loops, allowing 5 min. delay between the first and second tensioning. The energy recovered was expressed as a percentage of that expended.

## Results

The appearance of the treated yarn at different degrees of substitution is shown in Figure 2. At the higher substitutions, it will be noted that the yarn is distorted or snarled due to the large contraction during reaction without tension. This is a result of lateral expansion resulting in a relatively great increase of the effective twist.

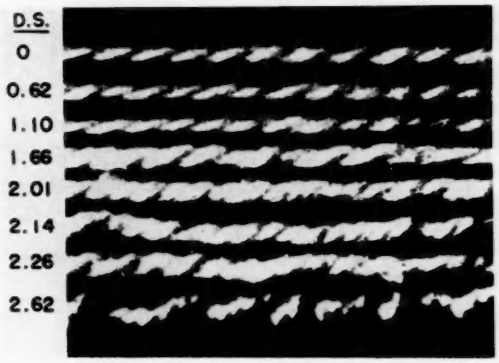


**Fig. 2.** Appearance of yarns of different degrees of substitution.

### *Changes in Molecular Structure*

*Density.* When the densities of cyanoethylated cotton yarns were plotted against the degree of substitution they fell at the points indicated by circles in Figure 3. The density is only slightly curvilinear with the substitution. A least square line fitted to the observed densities $d$ yielded the following equation:

$$d = 0.215 + \frac{8.7485}{DS + 6.5532}$$

where DS represents the degree of substitution. This equation is plotted as a smooth line through the observed points, Curve A.

A computation of density anticipated from consideration of the molar weights and volumes of cyanoethyl groups (density 1.0 assumed [4]) and cellulose( density 1.55 assumed) led to the equation:

$$d = 1 + \frac{1.0792}{DS + 1.9773}$$

which is plotted in Figure 3 as Curve B. This curve is below Curve C and somewhat below the observed values at low substitutions, but much too high at the higher substitutions. Of course, the density of the cyanoethyl groups, assumed to be 1.00, while reasonable, is completely arbitrary. However, when the density of these groups neces-

sary to yield the observed densities was calculated, it was found that it decreased progressively with substitution from 1.061 g./cc. at DS = 0.62 to about 0.923 at the higher substitutions, and average 0.967.

In order to compare these results with those of Grant et al. [7] a transformation in the latter is necessary. It was shown by Conrad [4] that the density found by Grant et al. was directly proportional to the cellulose content, abbreviated here, as $C$, in percent.

$$d = 0.934 + 0.00616C$$

It can be shown that the cellulose content is equal to $10{,}000/(100 + A)$, where $A$ is percent add-on in cyanoethylation. This value is related to degree of substitution

$$A = 32.73\text{DS}$$

so that we can derive

$$d = 0.934 + \frac{1.882}{\text{DS} + 3.055}$$

In Figure 3, Curve C, calculated from Grant's values, lies well above the observed densities except at the very lowest substitution. The samples in the present series are lighter than the samples measured by Grant et al., by as much as 7%. The reason for this discrepancy is not a difference of technique used for measuring the density.

There was also a difference in the experimental conditions of the reaction. Grant et al. used 2% sodium hydroxide generally, as catalyst, whereas 6% sodium hydroxide was employed in the present study.

The density of cellulose might vary between 1.497 g./cc. for amorphous and 1.583 g./cc. for crystalline cellulose, as proposed by Hermans [8]. At DS = 1.0, where apparently little, if any, loss of crystallinity occurs, the original crystallinity of cotton cellulose should be applied (about 70). At DS = 2.0, where x-ray tracings show crystallinity to be lost, it would be close to 0. By use of Hermans' densities and the density of 0.967 for the cyanoethyl group at DS = 1.0 and 2.0, the densities 1.388 and 1.275

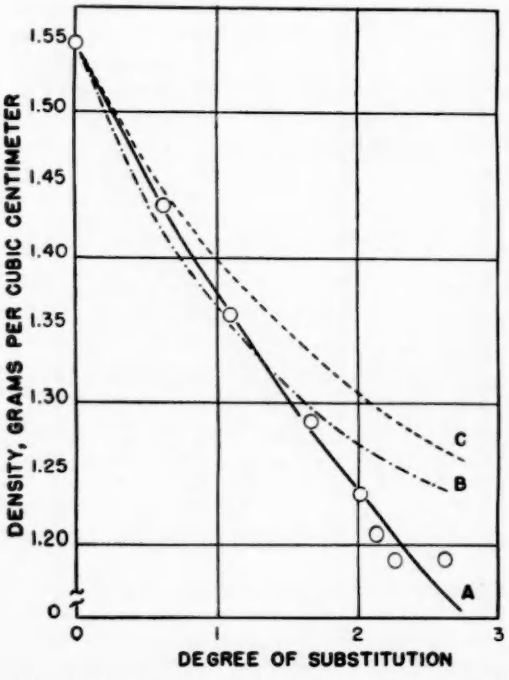


**Fig. 3.** Density of cyanoethylated cotton yarns (○). Curve A, least square fit to data; Curve B, densities computed from molar volumes and weights of components; Curve C, derived from data of Grant et al. [7].

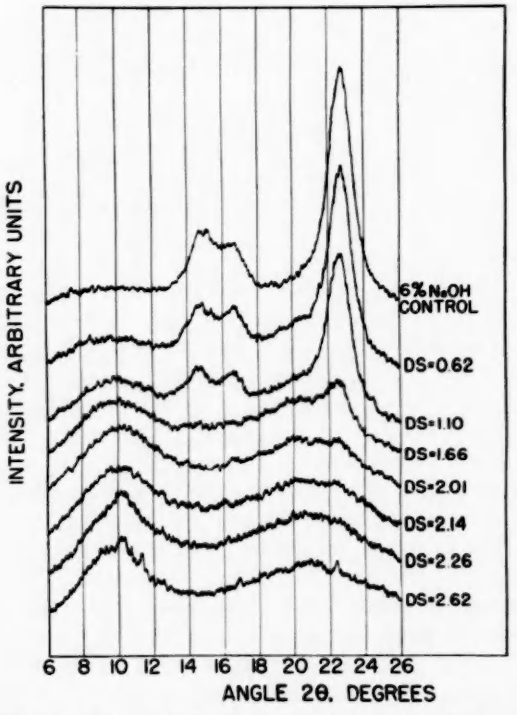


**Fig. 4.** Radial tracings of x-ray diffraction intensity from cyanoethylated yarns.

g./cc. were computed respectively. This gives a slightly higher molar density at the lower substitution but scarcely any improvement at DS = 2.0. Further consideration along these lines was not considered to be profitable at present.

*Crystal structure.* X-ray diffraction intensity traces of the different samples are arranged one below another in Figure 4. By reference to Figure 4, a rapid decrease will be noted in the height of the stronger (002) cellulose interference at $2\theta = 22.6°$, as previously observed by Segal and Conrad [11]. This reduction seems to be complete at a substitution of 2.01. The tracing represents here an essentially amorphous pattern. The native cellulose interferences at $2\theta = 14.8°$ and 16.6° have disappeared and a new diffuse diffraction halo appears at about $2\theta = 10.3°$. The latter becomes somewhat more distinct at higher substitutions and can be augmented by annealing for 30 min. at 175–180° C. (see Figure 5).

The changes of the x-ray diffraction can be more clearly seen by plotting the intensities of the curves at $2\theta = 10.3°$ (not annealed) and 22.6° as the substitution changes (see Figure 6). It is observed that the intensity of the native cellulose interference (002) at $2\theta = 22.6°$ decreases somewhat with increasing substitution to about 1.10, drops rapidly with further substitution to about 2, and then remains almost constant. The intensity for $2\theta = 10.3°$ of cyanoethylated cellulose, however, rises almost linearly with substitution. The substitution of about 1.10 may be considered to be at about the point where the amorphous, accessible regions, originally present in the cellulose of the fiber, are exhausted; further reaction necessitates encroachment on the crystalline region [6]. The rapid loss of the 002 peak of cellulose with further reaction supports this view. Furthermore, the gradual increase of the intensity maxima at $2\theta = 10.3°$ with substitution indicates some crystallization as substitution increases.

*Stress relaxation.* To clarify the molecular changes brought about by cyanoethylation without tension, stress relaxation was studied.

The curves representing the logarithm of stress versus temperature for each degree of substitution (exclusive of 0.62 and 2.14, for which samples were not included) are presented in Figure 7. It is seen that starting from 120 g. the yarn relaxes considerably in most cases between 20° and 70° C. It was determined in auxiliary experiments that the minimum which occurs in undried samples is due to moisture and can be prevented by predrying the yarns [14]. The stress of the unsubstituted sample, after passing through this minimum, decreases nearly linearly to about 40% of its initial value at 220° C.

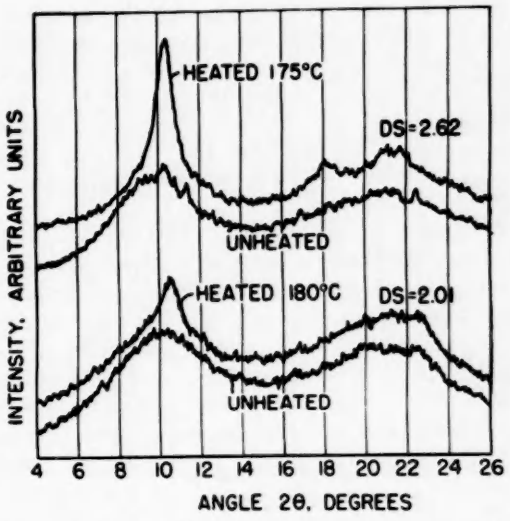


**Fig. 5.** X-ray intensity of yarns cyanoethylated to DS = 2.01 and 2.62 before and after annealing.

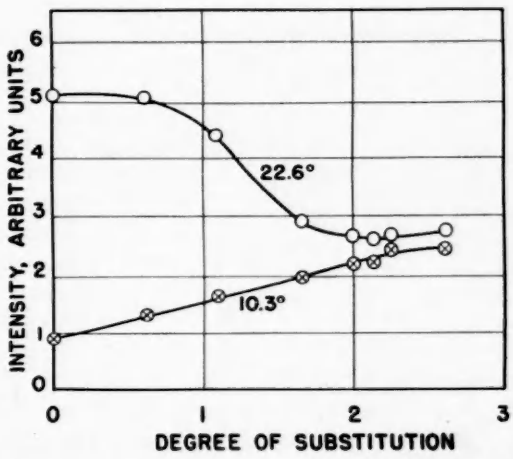


**Fig. 6.** Intensity of radial x-ray tracings at $2\theta = 10.3°$ and 22.6° of cyanoethylated yarns.

A substitution as low as 1.10 causes a large change in the stress relaxation, the stress at 210° C. now representing only about 5% of its value at room temperature. There are beginning evidences of a second order transition at about 140° C.

Further substitution to 1.66 yields a curve with a more evident second order transition at slightly lower temperature and a decided minimum relaxation at the highest temperature of 230° C. Substitution to 2.01 moves the relaxation curves slightly further to the left. It is at this point that x-ray tracings (Figure 4) indicate essentially complete loss of crystal structure.

The curves at substitutions of 2.26 and 2.62 show a change compared to those of the lower substitutions. The relaxation does not decrease so much at the higher temperatures; after having passed through a minimum, the stress rises again. This is interpreted to result from two processes occurring concurrently in the highly substituted, highly amorphous celluloses: first, the second order (glassy to rubbery) transition proceeds, but superimposed upon this is a rapid crystallization of the cyanoethyl cellulose at the higher temperature. A further increase of substitution from 2.26 to 2.62 appears to favor crystallization by raising the level of the minimum stress and by reducing the temperature to the minimum of the curve from 170° C. to 110° C.

A further confirmation of the above interpretation seems to be provided in Figure 8; the sample substituted to a degree of 2.01 was carried through a complete heating and cooling cycle. The heating portion of the curve reproduces the corresponding one in Figure 7. However, during the cooling portion of the cycle the stress developed at temperatures

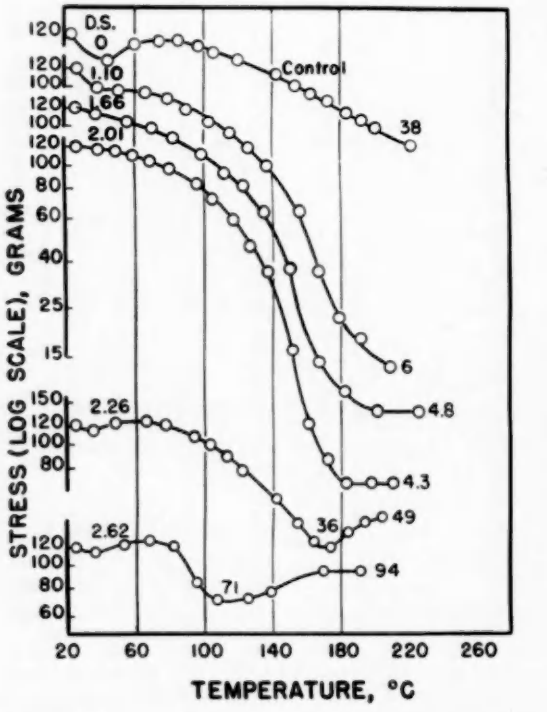


Fig. 7. Stress relaxation at different temperatures of cyanoethylated yarns. Numbers near and at right end of curves indicate stress at that point.

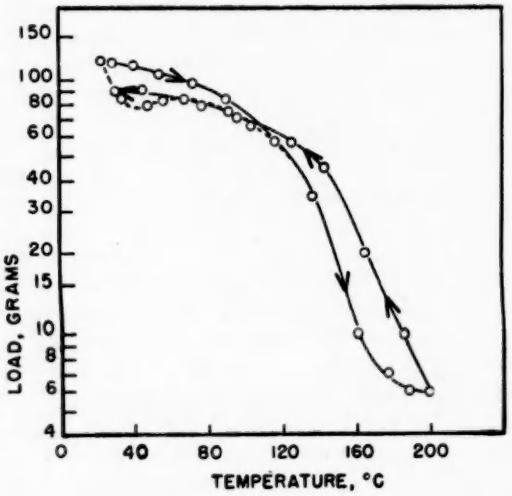


Fig. 8. Stress relaxation of cyanoethylated yarn (DS = 2.01) in a heating and cooling cycle.

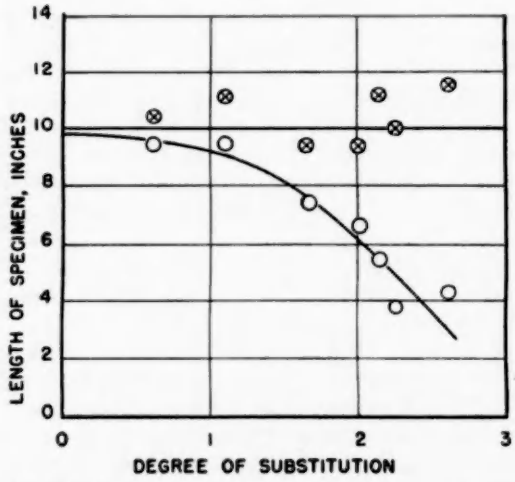


Fig. 9. Contraction and length at break of reacted yarns. Open circles indicate length after reaction; crossed circles indicate computed length at break.

above 110° C. is in all cases above that of the heating portion of the cycle, indicating increased order or crystallinity. Furthermore, while the curve during the heating portion of the cycle follows a long broad course, indicating a gradual change from the glassy to the rubbery state, the curve during the cooling cycle has a much sharper bend, which also occurs at a distinctly higher temperature. Finally, below 110° C. the cooling curve crosses over below the heating curve, confirming that a certain amount of relaxation or plastic flow has occurred at the higher temperatures.

Figure 8 also demonstrates the plasticizing effect of moisture. The dashed portion of the curve, with a minimum of about 46° C., represents the heating portion of the cycle with moisture present; it joins the smooth curve, representing a previously dried sample, at a temperature of about 120° C., where evaporation is practically complete.

### *Changes in Morphological and Mechanical Properties*

*Linear density, length, strength, and ultimate elongation.* As degree of substitution of cyanoethyl groups in the cellulose increases toward the possible maximum of 3 (one for each hydroxyl group in the anhydroglucose unit), changes occur in the morphological and mechanical properties. The linear density of the yarn increases rapidly (Table I). If substitution were the only cause for increase in linear density, the increase at a substitution of 3 would be 98%. As can be seen from the table, the weight has already increased beyond this at a DS of only 1.66, and at a DS of 2.62 the weight increase is already over 600% above that of the original yarn.

The increase in linear density is due, of course, to a large amount of longitudinal contraction. Up to a DS of 1.10, only a small contraction occurs (Column 3 of the table). But by the time the DS has reached 1.66, the contraction has increased to 25%; at the DS 2.26 it has exceeded 60%.

As substitution increases there is first a slight increase in breaking strength, followed by an essential decrease. The same trend is shown both by the bundle and single yarn tests.

With increasing substitution the ultimate elongation increases, up to the maximal substitution reached. It might be questioned whether the elongation increase is partly real or due merely to removal of contraction which occurred during reaction. This question was answered by taking into account the amount of contraction which occurred. The results are shown in Figure 9. It is seen that in spite of considerable scatter of the points representing the computed length at the rupture of the reacted yarns, they are practically identical to the length before contraction took place.

The tensile stiffness of the treated yarn (Table I) decreases greatly, as anticipated from the increase of elongation.

*Energy to rupture.* The energy to rupture of the yarns is shown in Figure 10, plotted in absolute units and in percent of that of the control. The energy, in comparison to the control, decreases considerably at DS values of 2 or less and also at the highest degree of substitution. However, a considerable increase over the control occurs at DS values of 2.14 and 2.26.

*Elastic recovery.* The tensile recovery of unreacted and reacted yarn, from 6% elongation, sub-

**TABLE I. Change of Physical Properties of Yarn with Degree of Substitution**

| Degree of substitution | Linear density increase, % | Linear contraction, % | Bundle breaking strength | | Yarn breaking strength | | Elongation at break, % | Tensile stiffness, g./tex |
|---|---|---|---|---|---|---|---|---|
| | | | Absolute, g./tex | Relative, % | Absolute, g./tex | Relative, % | | |
| 0* | 0 | 0 | — | — | 14.27 | 100 | 10.1 | 141 |
| 0† | 0 | 2.1 | 13.55 | 100 | 14.33 | 100 | 10.1 | 142 |
| 0.62 | 26.2 | 5.9 | 15.40 | 114 | 14.80 | 103 | 10.8 | 136 |
| 1.10 | 56.5 | 5.5 | 14.92 | 110 | 12.30 | 86 | 18.0 | 68 |
| 1.66 | 103.6 | 25.9 | 9.96 | 74 | 12.10 | 84 | 26.3 | 46 |
| 2.01 | 156.0 | 34.0 | 8.12 | 60 | 8.90 | 62 | 42.0 | 21 |
| 2.14 | 274.7 | 45.7 | 10.25 | 76 | 9.60 | 67 | 105.7 | 9 |
| 2.26 | 417.5 | 61.7 | 10.44 | 77 | 8.20 | 57 | 134.0 | 6 |
| 2.62 | 604.0 | 56.9 | 4.82 | 36 | 6.60 | 46 | 167.0 | 4 |

* Control yarn, untreated.
† Control, treated with 6% NaOH and toluene.

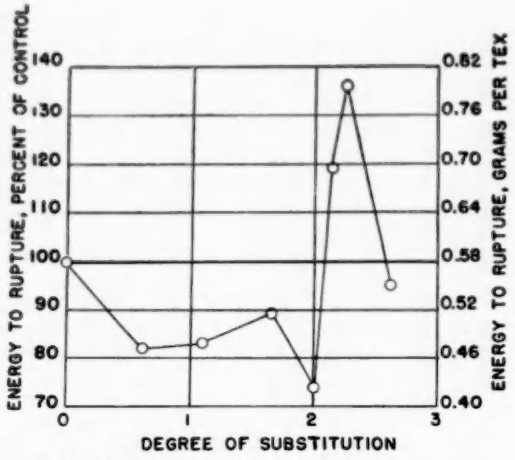


**Fig. 10.** Energy to rupture of cyanoethylated yarns.

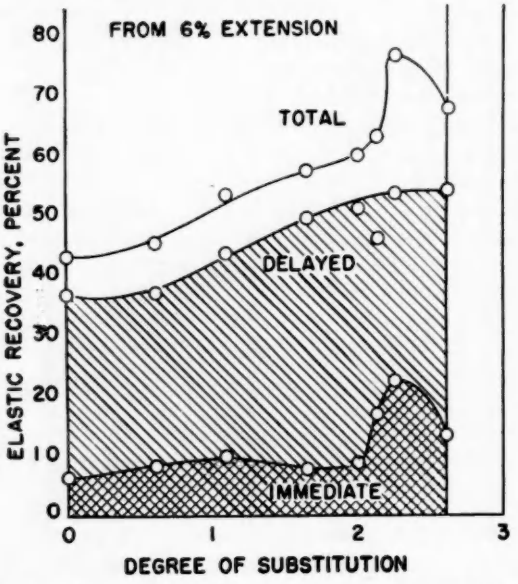


**Fig. 11.** Elastic recovery of untreated and cyanoethylated yarns from 6% extension.

divided into immediate and delayed portions, is shown in Figure 11. An absolute elongation of 6% is approximately 60% of the elongation of the control yarn. Since the results are based on the modified yarn, with greatly "increased" ultimate elongations as the DS exceeds 1.10, the result is to apply, relatively, a much smaller proportion of the ultimate elongation at successively higher degrees of substitution. This might account for the gradual upward

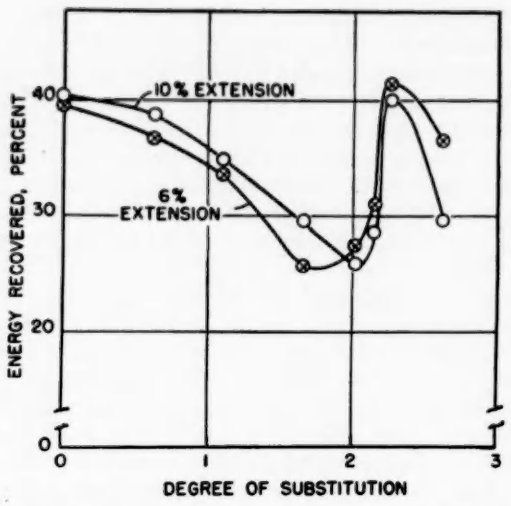


**Fig. 12.** Recoverable energy at 6% and 10% elongation of cyanoethylated yarns.

trend of the delayed and total recovery of extension up to a DS of 2.0. However, it does not seem to account for the sudden improvement in immediate elastic recovery between DS of 2.0 and 2.26. These occur at the same substitutions, where the highest energies for rupture were required.

*Recoverable energy.* The amount of energy recovered from 6% and 10% extension is shown in Figure 12. A downward trend is observed in both curves with increasing DS to about 2, followed by rather remarkable increases at DS of 2.14 and 2.26. The recovery at the latter is similar to that of the control.

## Discussion

The mechanical and molecular changes observed will, for convenience only, be discussed according to three regions of substitution. These are from DS = 0 to 1.10, from DS = 1.10 to 2.0, and above DS = 2. The results seem susceptible to interpretation along the following lines.

In the low substitution range, below DS = 1.10, reaction occurs almost, if not exclusively, in the preexisting amorphous regions and perhaps on the surfaces of the cellulose crystallites. Substitution in these regions may approach the maximum of three cyanoethyl groups per anhydroglucose unit, with little or no disturbance of the crystalline regions. The addition takes place with relatively little evident effect on the physical properties, with the exception

of tensile stiffness and energy to rupture, both of which decrease considerably. Changes in physical properties are essentially similar to those observed previously [4, 5] for comparable yarns in this range of substitution. Density decreases nearly linearly. The highly crystalline structure of the native cellulose is largely retained, as indicated by the x-ray diffractograms. The stress relaxation of the untreated fiber with increasing temperature is quite limited, showing no evidence of a transition from the glassy to the rubbery state.

In the range of substitution between DS = 1.10 and 2, a rapid change takes place in the molecular structure. The reaction has almost, if not completely, exhausted the amorphous regions originally present, and further reaction requires creation of new amorphous regions at the expense of the crystalline. In this range the interferences of the cellulose lattice disappear rapidly and practically completely and a new diffuse interference rises in the vicinity of $2\theta = 10.3°$, indicating minute or poorly developed crystalline domains.

The density of the reacted samples continues its nearly linear decline. As the temperature increases, the stress relaxation begins to show two rather distinct slopes, which intersect in the temperature region of 120–140° C., indicating a tendency toward transformation from a glassy to a rubbery state. The bend in the stress—temperature curves is not sharp, but is typical of such transformations in linear high polymers [2]. The stress at temperatures of 180° and higher decreases to as low as 4% of its value at room temperature, indicating a decreasing molecular cohesion of the cellulose chains and an increasing tendency to display "liquid behavior."

Large contraction occurs, together with a considerable reduction of tensile strength and stiffness and an increase in ultimate elongation. Energy to rupture continues low, and recovery decreases. Immediate elastic recovery remains relatively constant, but delayed recovery increases considerably, indicating the loosening of lateral bonding and a more mobile state of the molecules.

In the third stage of substitution, above DS = 2, the crystal structure of the native cellulose has been lost, and we have an amorphous cellulose ether, containing on the average two or more cyanoethyl groups for every anhydroglucose unit. The amorphous nature of this material is indicated by the appearance of a broad interference of low intensity, which does not change with further substitution. The new interference at $2\theta = 10.3°$ becomes sharp by annealing, indicating recrystallization of cyanoethyl cellulose.

The stress relaxation pattern with rising temperature shows further change. The temperature of the glassy–rubbery transformation decreases to about 70° C. at DS = 2.62. The stress relaxation does not decrease to as low a degree as in the two lower ranges of substitution, being followed at higher temperatures by a distinct restoration of stress with temperature. The rise of stress is indicative of crystallization at these higher temperatures, which is probaly promoted by stress. The complete cycle of stress relaxation as the temperature is increased and then decreased follows a curve during cooling which is nearly linear and, above the glassy transition temperature, is above the heating curve. This constitutes further evidence of the augmented crystalline structure of the heat-stressed yarn. Its transition temperature is also above that of the heating curve. In the glassy state region, the cooling curve of stress relaxation crosses over that of the heating curve due, presumably, to the small amount of molecular relaxation which has occurred.

The mechanical properties reflect the molecular changes. Large linear contraction occurs, manifested not only in the outward kinked appearance of the yarn but also in an enormous linear density increase.

Losses of tensile strength and stiffness continue while ultimate elongation increases. Interestingly, the energy to rupture, immediate elastic recovery and energy recovery all pass through maxima. It is not clear whether or not this could be an entropy effect associated with the amorphous state of the molecules in this region. Evidently, there is a gradual relaxation of the cohesive forces, and it is possible that these have decreased below their optimum value at the highest substitution. The practical implications in this direction may well deserve further consideration.

## Summary and Conclusions

Cotton yarns of 14/2 construction and normal twist (TM = 3.00) were cyanoethylated under special conditions, without tension, to various degrees of substitution up to DS = 2.62 and studied with particular reference to changes in the mechanical properties and molecular structure. The effect on

the properties could, for convenience of discussion, be divided into three regions of substitution.

Low substitutions (DS = 0–1.10), limited almost if not entirely to the noncrystalline regions of the cellulose, have led to a slight linear contraction, associated with a corresponding increase in ultimate elongation. Yarn linear density increases, due both to the contraction and to the cyanoethyl groups added. Breaking strength increases slightly, as does delayed elastic recovery. Both energy to rupture and tensile stiffness decrease considerably; energy recovery decreases slightly. The density of the fiber decreases with substitution, while the crystalline structure of the native cellulose shows little disturbance.

In the intermediate range of substitution (DS = 1.10–2.0), characterized by rapid and almost complete loss of the crystalline structure of the cellulose, linear contraction of the yarn becomes marked and the yarn number and ultimate elongation increase greatly. Breaking strength drops progressively and tensile stiffness continues its rapid drop. Energy to rupture holds steady but recovery decreases markedly. Immediate elastic recovery remains constant but delayed recovery improves somewhat. Density continues its linear decline. Stress relaxation with rising temperature shows two pronounced slopes, indicating a gradual transition from the glassy to the rubbery state. At the highest temperature (*ca.* 220° C.) stress at constant strain amounts to only about 4% of that at room temperature.

In the highest substitution range (above DS = 2.0), characterized by essentially amorphous cyanoethylated cellulose, linear contraction continues to about 40% of the original length, and the yarn displays a characteristic kinked appearance. Breaking strength and tensile stiffness decrease to their lowest values, and ultimate elongation increases to its highest. On the other hand, energy to rupture, immediate elastic recovery, and energy recovery pass through strong maxima. The absence of interferences in the x-ray tracings demonstrate the absence of crystalline structure, but annealing is now capable of developing a new crystal pattern of cyanoethyl cellulose with a peak at $2\theta = 10.3°$.

Stress relaxation with rise of temperature shows a gradually decreasing transition temperature and, at the higher temperature, a distinct increase of stress, indicative of crystallization.

## Acknowledgments

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# Reaction of Wool with Oxidizing Agents in Concentrated Salt Solutions

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**Abstract**

Concentrated salt solutions protect wool from oxidative degradation. Oxidizing agents produce a higher degree of shrink resistance in concentrated salt solutions than in the absence of salt. Many oxidations, followed by a reduction, shrinkproof wool when either treatment alone does not.

Results support the idea [20, 46] that attack on disulfide bonds is the only primary reaction during chemical shrinkproofing and that attack at some other point of the protein structure need not occur. However, breaking of disulfide bonds is not sufficient in itself to produce shrinkproofing effects, and the exact nature of chemical changes leading to shrinkproofing is unknown. No conclusive evidence has been found to decide whether or not changes in frictional properties are the general cause of shrinkproofing.

Evidence is given that, under conditions where swelling is less than in simple aqueous solutions, reaction still occurs throughout wool fibers rather than only at the surface.

The results do not agree with theories which suggest that shrinkproofing is due in some way to formation of degraded layers of protein material in wool fibers.

## Introduction

Most of the common oxidizing agents have been studied as possible shrinkproofing reagents, for example the free halogens [13, 17, 19, 21, 22, 23, 33, 39, 42, 50, 52, 55, 56], N-halogen compounds [2, 3, 17, 42, 51], permanganate in acid [5, 27] or neutral [49] solution, peroxide [12, 53], perborate [9], peracetic acid [54], persulfate [51], permonosulfuric acid [48], chlorite [16, 37, 40], bromic acid [28], and iodate [26]. Mixtures of oxidizing agents such as permanganate-hypochlorite [41] and peracetic acid-hypochlorite [14] are used industrially.

The reactions have been reviewed by Moncrieff [39] and Alexander and Hudson [7]. Oxidizing agents can cause severe degradation and, under some conditions, the wool may be completely dissolved. Recent studies on the alkaline degradation of wool showed that certain concentrated salt solutions exert a striking protective effect [36], and this suggested that wool may also be protected in this way from oxidative degradation. This paper gives the results of an investigation of this suggestion, with particular reference to the shrinkproofing effects produced by treatments with oxidizing agents in salt solutions.

Hirst and King [25] found that the rate of reaction of chlorine with wool was lowered by the addition of high concentrations of salts and also that less chlorine was then needed to produce a given degree of shrink resistance. The addition of oxidizing agents to solutions of inorganic halides or halogen acids would result, under certain conditions, in oxidation of halide ions to free halogen; Trotman [51] proposed this as a method for producing chlorine for shrinkproofing treatments. Such processes have been patented [8, 10, 29], and the use of activators for these oxidations has been investigated [16, 47].

## Experimental

### *Materials*

*Wool.* Unless otherwise stated, a scoured, plain-weave worsted fabric (33's and 30's Yorkshire skeins warp and weft respectively; 32 ends/in., 30 picks/in.) made from Merino 64's wool was used. Corriedale loose wool purified for single fiber experiments has been described [35], while Lincoln 36's loose wool used for friction measurements was purified similarly.

*Reagents.* All chemicals used were of ordinary laboratory reagent quality.

### *Methods*

*Fabric treatments.* In general, fabric samples weighing about 10 g. were treated at a liquor:wool

ratio of 20:1. Some experiments were also done in a laboratory winch machine of 3-l. capacity. Non-ionic wetting agents were found to have no effect on the reactions and were used throughout.

*Estimation of cystine, tyrosine, tryptophan, and primary amino groups.* The methods used have been described in detail [34].

*Alkali solubility.* This was determined by the method of Harris and Smith [24].

*30% Index.* This was determined by the method of Speakman [44].

*Friction measurements.* Coefficients of friction of Lincoln 36's fibers were measured by the capstan method of Lipson and Howard [30], fiber and keratin rod being lubricated with 0.05 *M* sodium borate solution containing 0.02% (vol./vol.) Teepol.

*Fabric properties.* Felting shrinkage, bursting strength, and reflectance were measured as previously described [34, 36].

## Results

### *Reaction of Wool with Chlorine in Concentrated Sodium Chloride Solutions*

A series of experiments was carried out in which fabric samples with calibrated fibers attached (i.e., fibers whose work to stretch 30% had been found) were treated with various amounts of chlorine at pH 2.0 for 30 min. at 25°. Some decomposition took place when sodium hypochlorite was added to the salt solutions, so that care was necessary to obtain solutions of the required concentrations. After treatment the wool was not given an antichlor but was washed thoroughly in running water for 24 hr.

Sodium chloride significantly retards the rate of degradation of wool by chlorine (Table I). All fabrics treated with 5% or 10% chlorine on the weight of wool showed zero shrinkage after prolonged machine washing. Compared with treatments in the absence of salt, wool treated in the salt solutions was not yellowed so much, had lower alkali solubility and weight loss, and had higher fabric bursting strength and fiber strength (Table I). The handle of fabrics treated in salt solutions, although harsh, was better than in the absence of salt.

Even with 10% chlorine on the weight of wool, no change in tyrosine or tryptophan was found, although cystine was extensively oxidized. This does not agree with Alexander and Gough [6] who, using Lugg's method, found losses of tyrosine. Chlorine, in the absence of salt, reacted with amino groups, so it was impossible to tell whether peptide bonds had been hydrolyzed during treatment. The results in salt solutions (Table I) indicate that it is unlikely that hydrolysis occurred during these treatments.

The reaction with hypochlorite in neutral or alkaline solution was not investigated in detail. Such treatments [13, 21, 22, 42] cause more yellowing than acid treatments and the pH is more difficult to control. Salt solutions again reduce the rate of degradation, results similar to those given in Table I being found for weight loss and yellowing.

### *Reaction of Wool with Oxidizing Agents in the Absence of Salts and Chloride Ions*

Optimum conditions of treatment were determined for each oxidizing agent (Table II). Reasonably good shrink resistance by oxidation alone was obtained with chlorine, perborate, acid bromate, and acid permanganate. Except for chlorine, these re-

**TABLE I. Properties of Wool Treated with Chlorine at pH 2.0 for 30 Min. at 25° in Presence and Absence of Sodium Chloride**

| Chlorine reacted with wool, % on wt. wool | Conc'n NaCl in solution, *M* | Wt. loss, % | Reflectance | Tyrosine, mole/$10^4$ g. wool | Tryptophan, mole/$10^4$ g. wool | Cystine, mole/$10^4$ g. wool | Primary amino groups, mole/$10^4$ g. wool | Alkali solubility, % | Bursting strength | | 30% Index† |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Conditioned* | Wet | |
| (Untreated wool) | | | (46) | (3.6) | (0.54) | (4.6) | (2.10) | (12) | (114) | (86) | (0.99) |
| 5 | — | 2.8 | 33 | | | 3.5 | 1.90 | 23 | 109 | 80 | 0.84 |
| 5 | 2.0 | 1.8 | 38 | | | | | | | | |
| 5 | 5.3 | 0.7 | 42 | 3.6 | 0.55 | 4.1 | 2.09 | 19 | 111 | 84 | 0.91 |
| 10 | – | 4.8 | 24 | 3.6 | 0.56 | 3.0 | 1.37 | 32 | 99 | 72 | 0.79 |
| 10 | 2.0 | 2.7 | 31 | | | | | | | | |
| 10 | 5.3 | 1.0 | 36 | 3.6 | 0.54 | 3.9 | 2.12 | 22 | 107 | 81 | 0.89 |

* Fabrics conditioned at 65% RH and 20° C.
† Ratio of work required to stretch fibers 30% after treatment to that required before treatment.

agents lowered the fabric bursting strength significantly. Alkali solubilities were increased, especially with acid bromate. The other oxidizing agents produced no significant shrink resistance, although bursting strengths were lowered and alkali solubilities increased.

Oxidized samples were also given a reduction aftertreatment with a 2% (wt./vol.) solution of sodium bisulfite. Treatment was for 30 min. at 25° using a 20:1 liquor:wool ratio. The reduction had no effect on wool oxidized under the conditions of Table II with chlorine, perborate, acid bromate, or acid permanganate, except to improve the color of acid bromate treated wool and to remove $MnO_2$ from the acid permanganate treated wool. However, when less chlorine was used, so that only moderate shrink resistance was obtained, a slightly improved shrink resistance was found after the oxidized wool had been treated with bisulfite. For example, treatment with 1% chlorine on the weight of wool gave a fabric which shrank 18% in the standard washing test, but a bisulfite aftertreatment brought the area shrinkage down to 14%. This effect was not observed with perborate, acid bromate, or acid permanganate treatments.

In agreement with the literature, it was found that a reduction aftertreatment has a profound effect on the degree of shrink resistance of wool oxidized with neutral permanganate [49] or permonosulfuric acid [48]. Fabric bursting strengths and alkali solubilities are changed slightly by the reduction (Table II).

Reduction significantly increases the shrink resistance of fabrics oxidized with acid chlorate, acid iodate, peracetic acid, or persulfate, the bursting strengths and alkali solubilities being little changed by the reduction. The degree of shrink resistance obtained with these four oxidizing agents is only moderate even when the wool has been extensively degraded (Table II).

Where the reduction aftertreatment has an effect on the shrink resistance of oxidized wool, the alkali solubility of the oxidized-reduced wool is lower than that oxidized only (Table II). This is not due to oxidized wool dissolving in bisulfite, since treatment as in Table II with permonosulfuric acid caused a 0.7% increase in weight while the reduction caused the oxidized wool to lose 0.6% in weight, which is much less than the 2% actual difference in alkali solubility between oxidized and oxidized-reduced samples. Similar results were found with persulfate treatments.

With neutral permanganate, the after-reduction appears to have two effects. First, precipitated $MnO_2$ is removed from the wool; second, reduction of the oxidized wool causes an increased shrink resistance. The $MnO_2$ on treated wool before reduction inhibits the shrink resistance of the oxidized wool, just as Farnworth (unpublished results) has observed with impurities such as wool wax or oils on fabrics shrinkproofed by reduction methods. For example, removal of $MnO_2$ by treatment with 1 $N$ $H_2SO_4$ for 4 hr. at 25° gave a fabric which shrank 23%, compared with 35% for a fabric treated simi-

**TABLE II. Reactions of Wool with Oxidizing Agents in the Absence of Salts and Chloride Ions**

| Oxidizing agent | Conc'n oxidizing agent, % of wt. wool | Conc'n $H_2SO_4$, $N$ | Temp., ° C. | Time, min. | Area shrinkage, % | | Bursting strength | | | | Alkali solubility, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Before reduction | | After reduction* | | | |
| | | | | | Before reduction | After reduction* | Conditioned† | Wet | Conditioned† | Wet | Before reduction | After reduction* |
| (Untreated wool) | | | | | (40) | (40) | (114) | (86) | (112) | (85) | (12) | (13) |
| Potassium bromate | 5 | 0.5 | 40 | 30 | 11 | 10 | 95 | 71 | 94 | 72 | 32 | 30 |
| Potassium chlorate | 200 | 1.5 | 80 | 60 | 37 | 22 | 97 | 68 | 94 | 64 | 60 | 57 |
| Potassium iodate | 10 | 1.0 | 80 | 60 | 35 | 25 | 85 | 61 | 87 | 63 | 60 | 58 |
| Peracetic acid | 10 | 0 (pH 2.7) | 40 | 30 | 38 | 18 | 95 | 67 | 91 | 64 | 47 | 44 |
| Ammonium persulfate | 100 | 1.0 | 40 | 30 | 34 | 20 | 96 | 70 | 96 | 71 | 22 | 19 |
| Potassium permanganate | 1 | 0.1 | 25 | 5 | 13 | 11 | 103 | 80 | 100 | 79 | 18 | 18 |
| Potassium permanganate | 5 | 0 (pH 7–7.5) | 50 | 30 | 35 | 9 | 100 | 78 | 96 | 76 | 24 | 20 |
| Sodium perborate | 20 | 0 (pH 10) | 70 | 60 | 4 | 4 | 96 | 75 | 95 | 74 | 22 | 24 |
| Chlorine | 3 | 0.05 | 25 | 15 | 11 | 11 | 112 | 85 | 112 | 85 | 20 | 20 |
| Permonosulfuric acid | 2 | 0 (pH 3) | 25 | 30 | 37 | 9‡ | 110 | 83 | 109 | 83 | 21 | 19 |

* Reduced with 2% (wt./vol.) sodium bisulfite at 20:1 liquor:wool ratio for 30 min. at 25°. This has no effect on the shrinkage of normal wool.

† Fabrics conditioned at 65% RH and 20°.

‡ Reduced with 10% $Na_2SO_3$ and 4% $NaHSO_3$ on wt. of wool for 30 min. at room temperature.

**TABLE III. Reactions of Wool with Oxidizing Agents in Hydrochloric Acid Solutions**

| Oxidizing agent | Conc'n oxidizing agent, % on wt. wool | Conc'n HCl, *N* | Temp., ° C. | Time, min. | Area shrinkage, % | | Bursting strength | | | | Alkali solubility, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Before reduction | | After reduction* | | | |
| | | | | | Before reduction | After reduction* | Conditioned† | Wet | Conditioned† | Wet | Before reduction | After reduction* |
| (Untreated wool) | | | | | (40) | (40) | (114) | (86) | (112) | (85) | (12) | (13) |
| Potassium bromate | 2 | 1.0 | 25 | 30 | 13 | 14 | 106 | 78 | 105 | 78 | 19 | 20 |
| Potassium chlorate | 100 | 1.0 | 60 | 30 | 11 | 9 | 100 | 72 | 99 | 71 | 22 | 22 |
| Potassium iodate | 5 | 1.0 | 60 | 60 | 14 | 12 | 79 | 59 | 78 | 60 | 52 | 50 |
| Peracetic acid | 10 | 1.0 | 40 | 60 | 31 | 23 | 98 | 70 | 94 | 67 | 43 | 42 |
| Ammonium persulfate | 50 | 1.0 | 40 | 30 | 17 | 15 | 98 | 72 | 98 | 73 | 22 | 22 |
| Potassium permanganate | 1 | 0.1 | 25 | 5 | 13 | 13 | 101 | 80 | 100 | 81 | 18 | 19 |

* Reduced with 2% (wt./vol.) sodium bisulfite at 20:1 liquor:wool ratio for 30 min. at 25°.
† Fabrics conditioned at 65% RH and 20°.

**TABLE IV. Reactions of Wool with Oxidizing Agents in Saturated Sodium Chloride Solutions**

| Oxidizing agent | Conc'n oxidizing agent, % on wt. wool | Conc'n $H_2SO_4$, *N* | Temp., ° C. | Time, min. | Area shrinkage, % | | Bursting strength | | | | Alkali solubility, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Before reduction | | After reduction* | | | |
| | | | | | Before reduction | After reduction* | Conditioned† | Wet | Conditioned† | Wet | Before reduction | After reduction* |
| (Untreated wool) | | | | | (40) | (40) | (114) | (86) | (112) | (85) | (12) | (13) |
| Potassium bromate | 1.5 | 0.075 | 25 | 30 | 6 | 6 | 114 | 86 | 113 | 85 | 16 | 16 |
| Potassium chlorate | 4 | 2.0 | 40 | 60 | 11 | 12 | 110 | 82 | 110 | 82 | 21 | 21 |
| Potassium iodate | 5 | 1.0 | 40 | 60 | 5 | 5 | 91 | 66 | 90 | 67 | 30 | 29 |
| Peracetic acid | 15 | 0 (pH 2.5) | 25 | 60 | 12 | 11 | 109 | 80 | 108 | 79 | 41 | 39 |
| Ammonium persulfate | 50 | 0 (pH 3) | 40 | 30 | 12 | 11 | 112 | 85 | 112 | 84 | 18 | 17 |
| Potassium permanganate | 1 | 0.1 | 25 | 5 | 9 | 8 | 112 | 84 | 113 | 84 | 16 | 16 |
| Potassium permanganate | 4 | 0 (pH 7) | 25 | 60 | 14 | 5 | 108 | 82 | 108 | 81 | 19 | 18 |
| Chlorine | 3 | 0.05 | 25 | 10 | 7 | 6 | 115 | 87 | 114 | 86 | 18 | 18 |

* Reduced with 2% (wt./vol.) sodium bisulfite at 20:1 liquor:wool ratio for 30 min. at 25°.
† Fabrics conditioned at 65% RH and 20°.

larly with permanganate but given no aftertreatment. The increased shrink resistance due to reduction of oxidized wool was observed by removing $MnO_2$ from a sample, treated as in Table II, by treatment with 5% bisulfite on the weight of wool for 30 min. at 25°. This white wool shrank 25%, compared with 35% for the fabric oxidized only, but on further treatment with a 1% (wt./vol.) bisulfite solution at a liquor:wool ratio of 20:1 for 30 min. at 50°, the area shrinkage of the fabric was 5%. Just as wool oxidized under given conditions shows increased shrink resistance with increasing severity of reduction, so more severe oxidation leads to better shrink resistance for a given reduction treatment. For example, wool oxidized with 3% permanganate on the weight of wool and then reduced with 10% bisulfite on the weight of wool shrinks 35% in the standard washing test, but a similar reduction of wool oxidized with 8% permanganate on the weight of wool gives a shrinkage of only 6%.

Farnworth (unpublished results) has found that extraction of all contaminants from woolen fabrics allows shrinkproofing effects to be obtained much more easily with chemical treatments. On such purified wool, treatment with acid bromate is an excellent shrinkproofing method. Treatment of unextracted wool with 2% potassium bromate on the weight of wool in 0.5 *N* $H_2SO_4$ at 40° for 30 min. gives a fabric with an area shrinkage of 27%, but on extracted wool the area shrinkage is 5%. Color is good, alkali solubility is 19%, and bursting strengths are decreased by 5%.

### *Reaction of Wool with Oxidizing Agents in Hydrochloric Acid Solutions*

Comparison of the results in Tables II and III shows that the acid permaganate treatment has a similar effect whether hydrochloric or sulfuric acid is used, in agreement with the results of Alexander, Carter, and Hudson [5]. Also, the peracetic acid

treatment in HCl is similar to that in the absence of acid, and a control experiment showed that treatment in $H_2SO_4$ was similar to these. Under the conditions used, therefore, reaction of permanganate and peracetic acid with wool must be faster than oxidation of chloride ions to chlorine.

With bromate, chlorate, iodate, and persulfate, better shrink resistance is obtained under milder conditions of treatment when HCl is used in place of $H_2SO_4$. This, together with the fact that reduction after oxidation has little effect on the shrink resistance (Table III), indicates that these treatments are probably chlorinations and that, under the conditions used, the rate of oxidation of chloride ions in solution must be greater than the rate of reaction of bromate, chlorate, iodate, or persulfate with wool.

*Reaction of Wool with Oxidizing Agents in Saturated Sodium Chloride Solutions*

The optimum conditions for treatments in saturated sodium chloride solutions differ from those already discussed and are given in Table IV. Treatments were carried out by adding concentrated solutions of the oxidizing agents to wool samples already wet out in the saturated salt. Permonosulfuric acid and perborate are omitted because shrinkproofing effects are not obtained with these reagents in saturated salt. In general, however, a higher degree of shrink resistance is obtained in the salt solutions with lower concentrations of oxidizing agents and less degradation. Even so, wool is still weakened and the alkali solubility markedly increased when it is treated with peracetic acid or acid iodate to give good shrink resistance.

Oxidized samples, treated as in Table IV, were also reduced with 2% (wt./vol.) sodium bisulfite solutions as described above. The reduction had a significant effect only on wool oxidized with neutral permanganate, better shrink resistance being produced with little change in fabric bursting strength or alkali solubility (Table IV).

Except for neutral permanganate, the reactions are different when the oxidizing agent is added to the acidified salt solution before the wool. Here, free chlorine may be produced, either by allowing the solutions to stand or by heating, so that a simple acid chlorination occurs when wool is added. In the above experiments, chlorine is produced relatively slowly in the presence of the wool.

If the oxidizing agent is added before the wool, much lower concentrations may be needed for a given degree of shrink resistance to be obtained. For example, 2% peracetic acid on the weight of wool to be treated, added to saturated sodium chloride and allowed to stand for 30 min. at 25°, produces about 2% chlorine on the weight of wool. Satisfactory shrinkproofing (11% area shrinkage in the standard washing test) is then obtained by treating a fabric in this solution. However, if peracetic acid is added to the wool wet out in the salt solution, the peracetic acid reacts simultaneously with wool and chloride ions, resulting in a combined treatment. Wool is degraded more in this way than by a simple treatment with chlorine to give the same shrink resistance (Table IV).

*Reaction of Wool with Oxidizing Agents in Concentrated Solutions of Salts other than Sodium Chloride*

The effects of two neutral salts on the oxidation of wool were briefly investigated. Sodium nitrate was taken as an example of a highly soluble salt and sodium sulfate as a moderately soluble one. In the first series of experiments, treatments were carried out either in neutral solutions or in solutions acidified with $H_2SO_4$, so that halide ions were absent. With the exception of chlorine, where the presence of sodium sulfate had little effect, the reactions of the oxidizing agents listed in Table II were slower in saturated sodium sulfate than in the absence of salts. Sulfate has a similar effect on the reaction of bromate–bromide solutions with wool [47]. In the present experiments, set up according to the conditions of Table II, the area shrinkage of a fabric treated with acid bromate in saturated sulfate was 25%, the alkali solubility being 16% and the bursting strengths the same as original. After a 4-hr. treatment, the area shrinkage was 17%; satisfactory shrinkproofing was not obtained even when the time of treatment was increased further. In general, sodium sulfate acted like sodium chloride and reduced the extent of degradation for a given degree of shrink resistance with all the oxidizing agents.

Apart from peracetic acid, reactions of the oxidizing agents in saturated sodium nitrate were intermediate in rate between those in sulfate and in the absence of salts. Again, degradation was less for a given shrink resistance in saturated nitrate solutions than in the absence of salts. A different reac-

**TABLE V. Solubility Measurements on Shrinkproofed Fabrics**

| Shrinkproofing treatment | Alkali solubility, % | Soap solubility, % | Lissapol N solubility, % |
|---|---|---|---|
| (Untreated wool) | (12) | (1.2) | (1.0) |
| Acid bromate/sodium chloride, as in Table IV | 17 | 2.6 | 1.0 |
| Neutral permanganate/sodium chloride, as in Table IV | 18 | 2.3 | 1.0 |
| Permonosulfuric acid, then bisulfite, as in Table II | 21 | 2.5 | 1.1 |
| 2% Permanganate + 2% active chlorine [41] | 20 | 3.2 | 1.2 |
| 1% Peracetic acid + 2% chlorine [14] | 20 | 2.9 | 1.0 |

**TABLE VI. Effect of Prior Boiling of Wool in Acid Solutions on Shrinkproofing Treatments in Saturated Sodium Chloride**

Fabric samples were boiled at 30:1 liquor:wool ratio in distilled water containing 15% $H_2SO_4$ on wt. wool; pH was 1.1.

| Time of boiling, hr. | Shrinkproofing treatment* | Area shrinkage, % |
|---|---|---|
| | | (40) |
| — | 1% bromate | 14 |
| 1 | 1% bromate | 15 |
| 3 | 1% bromate | 25 |
| — | 2% bromate | 3 |
| 1 | 2% bromate | 3 |
| 3 | 2% bromate | 9 |
| 3 | 3% bromate | 4 |
| — | 4% permanganate | 5 |
| 3 | 4% permanganate | 10 |
| 3 | 6% permanganate | 6 |

* Conditions of treatment as in Table IV.

tion must take place with peracetic acid in saturated sodium nitrate solution. The efficiency of peracetic acid as a shrinkproofing reagent is greatly increased, and treatment as in Table II with peracetic acid in saturated nitrate followed by 2% (wt./vol.) sodium bisulfite gives an excellent shrinkproofing effect. The area shrinkage of the fabric is 4% and alkali solubility 19%; conditioned and wet bursting strengths are 112 and 84 respectively.

Permanganate reacts in a similar way in all three salt solutions, producing a shrinkproofing effect, without an aftertreatment, under conditions where there is practically no effect in the absence of salts (*cf.* Tables II and IV).

In a second series of experiments, treatments were carried out in saturated sodium sulfate solutions acidified with HCl. With permanganate and bromate, reactions were slightly slower in the sulfate solutions, but with chlorate, iodate, peracetic acid, and persulfate, the reactions were much slower. For example, treatment under the conditions of Table III with chlorate in saturated sulfate gave fabrics with an area shrinkage of 32%; with iodate, 27%. If the time of treatment with chlorate were increased to 2 hr., the area shrinkage was 24%. Satisfactory shrinkproofing was not obtained under any conditions in the saturated sulfate solutions but, again, fabrics were less degraded in the sulfate solutions for a given degree of shrink resistance than in the absence of salt.

*Solubility Measurements on Shrinkproofed Fabrics*

Fabrics were treated with acid bromate/sodium chloride and neutral permanganate/sodium chloride as in Table IV, with permonosulfuric acid followed by bisulfite as in Table II, with 2% permanganate and hypochlorite containing 2% active chlorine [41], and with 1% peracetic acid and hypochlorite containing 2% active chlorine [14]. The solubilities in 0.1% (wt./vol.) soap solution or in 0.1% (wt./vol.) Lissapol N solution at 50° for four quarter-hour periods, each followed by washing with 2 l. distilled water on a Gooch crucible, were then determined.

The shrinkproofed fabrics are more soluble in soap, but not Lissapol N, than untreated fabrics (Table V). Most of the weight loss in soap occurs in the first quarter-hour treatment, the weight losses of shrinkproofed wool from then on being close to those (both about 0.3%) for normal wool during each treatment.

*Effect of Prior Boiling in Aqueous Solutions on Certain Shrinkproofing Treatments*

Prolonged boiling in acid solutions has an adverse effect on the degree of shrink resistance obtained under a given set of conditions with acid bromate/sodium chloride or permanganate/sodium chloride (Table VI). Increasing the concentration of reagent allows satisfactory shrinkproofing to be obtained on the acid-boiled fabrics (Table VI).

The only chemical changes to be expected in fabrics boiled in acid are hydrolysis of primary and secondary amide bonds and, possibly, loss of trypto-

phan. Estimation of tryptophan on the intact wool [34] showed that no changes (within ± 5%) had occurred during the 3-hr. boiling.

Boiling at pH values 2.5–7.0 has a smaller effect on the acid bromate/sodium chloride treatment and no effect on the permanganate/sodium chloride treatment. For example, treatment with 2% bromate after 3 hr. of boiling at pH 7 gave a fabric of 6% area shrinkage in the standard washing test. Above pH 7, the adverse effects of boiling begin to increase again, as has been shown by Farnworth, Neish, and Speakman [20].

*Friction Measurements*

The anti-scale frictional coefficient ($\mu_1$), the with-scale frictional coefficient ($\mu_2$), and the directional frictional effect (DFE) are unaltered by acid boiling (Table VII), so that the increased concentration of reagent needed to produce a given degree of shrinkproofing is not related to frictional properties of acid-boiled wool.

Chlorination by the acid bromate/sodium chloride treatment results in the well-known (e.g., [1, 22, 30, 38, 43]) increase in $\mu_1$ and $\mu_2$ and decrease in DFE (Table VII), the increased frictional coefficients resulting in the practical disadvantage of harsh handle.

Neutral permanganate treatment in water, under conditions where shrinkproofing is obtained in concentrated sodium chloride solution, changes the frictional properties but does not shrinkproof. The treatment in sodium chloride raises $\mu_2$ without changing $\mu_1$ and thus reduces, but does not remove, the DFE (Table VII). Wool is shrinkproofed by this procedure, but the handle is indistinguishable from untreated wool. Treatment with permonosulfuric acid followed by bisulfite has a similar effect.

## Discussion

The present results show that concentrated salt solutions protect wool from oxidative degradation (Table I) and that lower concentrations of oxidizing agents are needed in salt solutions for a given degree of shrink resistance to be obtained (Tables II and IV). The practical significance of these results is discussed in a subsequent paper.

Shrinkproofing effects have been obtained with no detectable changes in amino acids other than cystine and with no evidence for simultaneous peptide bond hydrolysis. With sodium hydroxide in concentrated salt solutions [36], again only cystine is attacked, although hydrolysis is possible. Farnworth (unpublished) has shown that thioglycollate treatment followed by mild hydrolysis shrinkproofs wool under conditions where neither treatment alone is effective, but also has found that bisulfite or thioglycollate treatments alone, under conditions (35°, pH 5–7) where hydrolysis is most unlikely, can cause shrinkproofing. The conclusion [30, 46] that the only primary chemical reaction taking place during shrinkproofing is attack on disulfide bonds is therefore supported by these results, and there

**TABLE VII. Frictional Coefficients and DFE of Shrinkproofed Fibers**

$\mu_1$ and $\mu_2$ are the anti-scale and with-scale coefficients of friction respectively; the differential frictional effect (DFE) is $\frac{\mu_1 - \mu_2}{\mu_1 + \mu_2}$.

| Treatment | $\mu_1$* | $\mu_2$* | DFE* | Cystine, mole/$10^4$ g. wool |
|---|---|---|---|---|
| (Untreated wool) | 0.39 ± 0.03 | 0.25 ± 0.01 | 0.22 ± 0.03 | 4.6 |
| Boiled 6 hr. as in Table VI | 0.38 ± 0.03 | 0.24 ± 0.01 | 0.23 ± 0.03 | |
| Acid bromate/sodium chloride as in Table IV | 0.48 ± 0.03 | 0.44 ± 0.02 | 0.04 ± 0.02 | |
| Neutral permanganate/sodium chloride† | 0.40 ± 0.03 | 0.31 ± 0.02 | 0.13 ± 0.02 | 4.3 |
| Neutral permanganate/water† | 0.39 ± 0.03 | 0.29 ± 0.02 | 0.15 ± 0.02 | 4.3 |
| Permonosulfuric acid, then bisulfite, as in Table II | 0.39 ± 0.03 | 0.32 ± 0.02 | 0.10 ± 0.02 | |

* Means and standard errors from values found with 10 fibers.

† Treated either in sodium chloride as in Table IV, or in water under the same conditions, followed by reduction with 5% sodium bisulfite on the weight of wool. Fabric treated in sodium chloride had an area shrinkage of 6%; that in water, 33%.

is no need to postulate that attack at some other point *must* occur [4], although this *may* undoubtedly take place in many shrinkproofing treatments.

However, the breaking of disulfide bonds is not sufficient in itself to produce a shrinkproofing effect, since hydrogen peroxide, peracetic acid [4], and certain other oxidizing agents (Table II) can attack disulfides extensively without causing shrinkproofing. Also, the loss of cystine is the same for permanganate treatments in sodium chloride or in water (Table VII); yet the former but not the latter shrinkproofs the wool.

The relationship of attack on disulfide bonds to the "shrinkproofing effect" is unknown. It has been suggested that dissolution of the cuticle is the reason for effective reactions [4], but microscopic evidence [11, 14, 22] is against this as a general explanation, and we have found that permanganate/sodium chloride-treated Merino fibers are indistinguishable from untreated under the optical microscope. Shrinkage, and shrinkproofing effects, appear sometimes to be related to frictional properties of wool fibers [1, 22, 30, 38, 43], although in at least one case [32] none of the properties usually thought to influence shrinkage were altered by an effective shrinkproofing treatment. Further, permanganate/sodium chloride treated fibers still have an appreciable, although reduced, DFE. Even if the DFE were the determining factor, there is no obvious way of explaining how the shrinkproofing reagents bring about the changes in DFE. Statements to the effect that disorientation of molecules in the scales changes frictional properties and causes shrinkproofing (e.g., [1]) are not satisfying explanations. In any case, oxidizing agents might attack cortex preferentially, since unreactive epicuticle material can be recovered from oxidation treatments which completely dissolve cortex [18]. There is no fundamental information as to how shrinkproofing reagents can change the frictional properties of wool (change in scale structure need not be detectable [11, 14, 22] and present work) or as to whether this is really the general cause of shrinkproofing.

Another proposed mechanism of shrinkproofing is that a gelatinous layer of degraded wool is formed immediately beneath the cuticle [45] and that swelling of this layer in acid or alkaline solutions prevents felting. However, fabrics shrinkproofed during the present work do not felt in cold water in a washing machine when normal wool does. The increased alkali solubility of wool could mean a loss of protein material during washing, especially in alkaline solution, and this may in some way cause non-felting. However, shrinkproofed wool is more soluble in soap than normal wool (Table V), but not in detergent solution, and again treated wool does not felt in these latter solutions. These results would be against Earland's [15] idea that some oxidizing agents are more effective than others because they allow dispersion or gelatinization of a layer of wool in the washing liquors.

A feature of the present results which has been observed previously [48, 49] and which is unexplained is that an oxidation followed by a reduction may shrinkproof where either treatment alone does not.

Yet another unexplained result is the adverse effect of acid boiling on subsequent shrinkproofing treatments (Table VI). This is not due to changes in frictional properties and probably not due to changes in amino acid content. It is possible that peptide bond hydrolysis is the cause, but this argument cannot go further when the shrinkproofing mechanism is unknown. The adverse effect of prior boiling at pH values above 7 can be explained [20] by a change of cystine into lanthionine, preventing the usual "shrinkproofing reaction."

These studies on salt solutions started with the idea that the decreased swelling [35] would help confine reaction to the fiber surface and result in more efficient shrinkproofing treatments [36]. The present results agree with the work on sodium hydroxide solutions [36] that, even although more efficient shrinkproofing treatments are obtained, this is probably not due to reaction being confined to surface layers of wool. Increased alkali solubilities and decreased cystine contents (which are the same for permanganate/sodium chloride and permanganate/water treated wools) mean that reagent has penetrated the fibers in salt solutions. It has been suggested that salt solutions and alcohol protect wool by slowing the rate of degradation, due to reaction products being insoluble in the solutions [36], and still allow the "shrinkproofing reaction" to occur. However, it is difficult to understand the effects of various salt solutions on peracetic acid and on neutral permanganate treatments and on neutral permanganate treatments where salt solutions appear to promote the "shrinkproofing reaction." No explanation is offered for permanganate treatments in concentrated solutions of various salts being rela-

tively so effective compared with other permanganate solutions.

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# Shrinkproofing of Wool with Neutral Permanganate or Acid Bromate in Concentrated Sodium Chloride Solution

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**Abstract**

Two shrinkproofing processes of possible industrial value are described. Each may be used continuously or as a batch process.

Treatments are with neutral permanganate (4–6% potassium permanganate on weight of wool) or acid bromate (1–2% potassium bromate on weight of wool) in concentrated sodium chloride solutions, the latter resulting in a chlorination which is more easily controlled to give even treatment than simple acid chlorinations. Batch processes are carried out at 20–40° C. in normal mill equipment, total processing times being 1–2 hr. Each process produces shrinkproofed wool at relatively low cost with no adverse effects of practical significance, although the acid bromate treatment requires a final softening. Permanganate/salt treatment requires no analytical control, causes no problems with fumes, gives even treatments so that there is no difficulty in piece dyeing after shrinkproofing, and does not yellow or alter the handle of the wool.

## Introduction

Relatively few shrinkproofing treatments have been used industrially. The cheapest and still most widely used is chlorination, particularly the simplest acid chlorinations (e.g., [22]). Mixed bath treatments with hypochlorite in near-neutral solutions, together with either permanganate [25] or peracetic acid [7], are also in use, as is the recent permonosulfuric acid treatment [27]. Provided that acid-chlorinated fabrics are softened with any of the effective agents now available, all of these methods are capable of giving shrinkproofed wool with little detectable change in color, handle, or fabric strength.

This paper describes further studies on two promising shrinkproofing treatments found during investigations of the reaction of wool with oxidizing agents in concentrated salt solutions [21]. One is with neutral potassium permanganate in concentrated sodium chloride solution and the other is with acid bromate in concentrated sodium chloride solution. These treatments have advantages over previous processes involving permanganate in the absence of salt [28], or acid bromate in chloride solutions of much lower concentrations [16] and may prove to be useful industrially.

## Experimental

### *Materials*

*Wool.* Unless otherwise stated, a scoured, plain-weave worsted fabric made from Merino 64's wool was used [21]. Corriedale loose wool used for single fiber experiments has been described [19].

*Fabric treatments.* Fabrics were treated either in a laboratory winch machine of 3-1. capacity or in stainless steel industrial dye winches.

*Analytical methods.* Total oxidizing power in bromate–chloride solutions was measured by titration, with standard sodium thiosulfate, of the iodine liberated from potassium iodide in 1–2 $N$ $H_2SO_4$. Permanganate was estimated by the standard titration procedure with hydrogen peroxide. Cystine, tyrosine, tryptophan, and primary amino groups were estimated as previously described [19].

*Rate of dye absorption or desorption.* This was measured in an apparatus as described by Armfield [2].

*Rate of wetting.* This was determined by Farnworth's modification [10] of the Draves test.

*Alkali solubility.* This was determined by the method of Harris and Smith [13].

*30% Index.* This was determined by the method of Speakman [26].

*Fabric properties.* Felting shrinkage, bursting strength, abrasion resistance, and reflectance were measured as previously described [20].

*Top shrinkage.* Samples of top, about 20 cm. long, were sewn near each end. The percentage change in length after rotating in 0.05% soap solution in glass tubes attached to a wheel was then found. The test was run until untreated top shrank 40%.

## Results

### *Treatments in Winch Machines with Permanganate in Concentrated Sodium Chloride Solutions*

Table I summarizes the important results from experiments in a laboratory winch machine. Times of treatment are suitable for industrial use. Solutions were unbuffered, the initial pH being 6.8 and the final pH 7.2. The pH can be varied within wide limits (pH 5–9) without substantially altering the rate. The pH of the bath gradually rises to about 7.6 after six consecutive treatments in the same liquor, and the use of a standing bath has been found to raise no problems.

The time of treatment can be decreased, if required, by lowering the pH below 5 by addition of acetic acid, for example. Alternatively, the temperature can be raised to 30–40°. The concentration of salt is not critical, but is best kept above 4 *M*. This is easily measured with sufficient accuracy by a hydrometer. Tests on a wide range of fabrics have shown that 4–6% potassium permanganate on the weight of wool is usually required.

The reduction to remove $MnO_2$ from the wool improves somewhat the shrink resistance of wool oxidized in salt; e.g., from about 14% area shrinkage to 7% [21]. The conditions of clearing can be varied widely, since the purpose is mainly to remove $MnO_2$ and not to develop the shrink resistance, as is the case with some other treatments [21]. Clearing with 5% sodium bisulfite on the weight of wool in 0.05 *N* $H_2SO_4$ takes about 30 min. at room temperature, but the time can be reduced by increasing the concentration of bisulfite or acid, or by warming. Clearing can be done in a few seconds by passing the wool through a 4–5% (wt./vol.) bisulfite solution. In practice this can be done continuously or by use of another standing bath.

The reaction in strongly acid solution is too rapid for an industrial batch process [1], and this outweighs the advantage of using less permanganate. The rate is also greater in strongly alkaline than in neutral solution; for example $t_{\frac{1}{2}}$ at 20° at pH 10 in saturated salt is 4 min. The wool is slightly yellowed in such a treatment (reflectance 42 compared with 46 for untreated) and is shrink resistant (area shrinkage 4% after treatment with 4% permanganate), but a similar treatment in the absence of salt causes more yellowing (reflectance 35) without producing a shrinkproofing effect under the clearing conditions in Table I.

Evenness of treatment was tested by dyeing lengths of treated fabric (8 ft. × 6 in.) in a solution of Naphthalene Scarlet 4RS (1% dye, 3% $H_2SO_4$, and 6% Glauber's salt, all on wt. wool) at 50° for 5 min. When $t_{\frac{1}{2}}$ for permanganate treatment was 4 min. or longer, dyeing was even, but there was a slight tendency toward unevenness for faster reactions. Industrial experience has shown that dyeing after these shrinkproofing treatments raises no prob-

**TABLE I. Treatment of Wool with 4% Potassium Permanganate (on the Weight of Wool) in Laboratory Winch Machine**

Liquor:wool ratio 20:1; pH 6.8–7.1; fabrics aftertreated with 5% sodium bisulfite on the weight of wool in 0.05 *N* $H_2SO_4$ until white.

| Conc'n sodium chloride, *M* | Temperature, °C. | $t_{\frac{1}{2}}$, min. | Area shrinkage, % | Alkali solubility, % | Bursting strength | | Reflectance |
|---|---|---|---|---|---|---|---|
| | | | | | Conditioned* | Wet | |
| (Untreated wool) | | | (40) | (12) | (114) | (86) | (46) |
| — | 20 | 26 | 30 | 19 | 110 | 80 | 42 |
| 3 | 20 | 24 | 9 | 20 | 108 | 80 | 45 |
| 4 | 20 | 23 | 6 | 19 | 108 | 81 | 47 |
| 5 | 20 | 23 | 5 | 18 | 108 | 80 | 47 |
| 5 | 30 | 10 | 6 | 18 | 108 | 80 | 47 |
| 5 | 40 | 4.5 | 5 | 19 | 108 | 80 | 47 |

* 65% RH, 20° C.

lems. This is probably because, even if uneven treatments are obtained, the increased rate of dyeing of the more heavily treated parts of fabric is relatively low (see Table III). Dyeing after shrinkproofing has little effect on shrink resistance except for some chrome dyeings, where area shrinkages may increase from 5% to about 9% in the standard test.

Frictional measurements [21] have shown that permanganate/salt treatments increase the with-scale frictional coefficient but do not change the anti-scale coefficient. This is probably why the handle of such treated fabrics is indistinguishable from untreated, which is a distinct advantage of permanganate/salt treatments over acid or dry chlorinations.

The results in Table I show that wool shrinkproofed with permanganate/salt is a little whiter than untreated. Bursting strengths are lowered by 5–8% and the alkali solubility is moderately increased. Analyses show that tyrosine, tryptophan, and primary amino group contents of wool are unaltered by the treatments and that cystine is reduced by 7%. The 30% index of treated fibers is 0.94.

*Treatments in Winch Machines with Acid Bromate in Concentrated Sodium Chloride Solutions*

Optimum conditions at 20° were determined in a laboratory winch machine. Some results with 1.5% potassium bromate on the weight of wool are summarized in Table II and may be compared with treatments where chlorine was produced by the addition of sodium hypochlorite to acid solutions.

Evenness tests with Naphthalene Scarlet 4RS showed that treatments were even if $t_{\frac{1}{2}}$ for oxidation were 8 min. or longer. That is, acid chlorine treatments in the presence or absence of salt resulted in the well-known (e.g. [22]) rapid and uneven dyeing after shrinkproofing, as did the reaction of bromate in 0.2 *N* acid. However, treatments with bromate at 0.1 *N* or lower acid concentrations resulted in even treatments and are suitable for industrial use.

The salt concentration should be at least 4 *M* to obtain the highest degree of shrink resistance for the lowest concentration of potassium bromate (desirable economically) at the fastest times giving even treatments.

Treatments with potassium bromate in HCl can be satisfactory [4], but are uneconomical due to the high concentration of bromate required. Treatments with 1.5% potassium bromate on the weight of wool were not satisfactory, even in 1 *N* HCl, if salt were omitted (Table II), although bursting strengths were down 7%, alkali solubility was 20%, and the fabric was light brown.

The color of acid bromate/salt treated wool is the same as untreated, but a normal antichlor with 1–2% sodium bisulfite on the weight of wool whitens the fabric slightly, reflectance increasing from 46 to 48. A reduction aftertreatment also decreases the rate of yellowing of the shrinkproofed wool during washing in alkaline solutions. For example, the reflectance of a fabric not given an antichlor dropped from 46 to 38 in the standard washing test, but that of a fabric aftertreated for 15 min. at 20° with 2% bisulfite on the weight of wool dropped only from 48 to 44.

Bursting strengths are virtually unaltered by acid bromate/salt treatments and the alkali solubility is moderately increased (Table II). Tyrosine, tryptophan, and primary amino group contents of wool were unchanged by the treatments but cystine was reduced by 10%. The 30% index of treated fibers was 0.93.

Frictional measurements [21] showed that both anti-scale and with-scale coefficients are increased and the DFE almost completely lost. This is a well-established effect of acid chlorinations (e.g., [12, 17]) and results in a harshened handle, although the handle of acid bromate/salt treated wool is better than acid chlorinations carried out in the absence of salt. The handle of worsted fabrics made from tightly twisted yarns is less noticeably affected than woolen materials and may not require softening. Normally, most fabrics would need to be softened, and satisfactory results have been obtained with a wide range of softening agents at 0.2–1% concentration on the weight of wool. Softening agents at concentrations up to 5% on the weight of wool have no effect on the shrink resistance of treated fabrics.

Industrial trials have shown that conditions of treatment are not too critical. The acid concentration can be between 0.075 and 0.10 *N* if the fabric is to be dyed afterwards, but if dyed fabrics are being treated this can be higher for quicker treatments. Salt concentrations need to be about 4 *M* or greater and are easily measured with a hydrometer. The use of a standing bath of concentrated salt is necessary for economy and presents no diffi-

culties, 20 successive treatments having been satisfactorily carried out in one trial. Wool sorbs approximately 5% by weight of the sulfuric acid added, and this amount is added to the bath after each batch of wool has been treated. The potassium bromate concentrations needed for various fabrics are between 1 and 2% on the weight of wool, no fabric yet tested having been found to require more than 2%.

*Properties of Wool after Shrinkproofing by Various Methods*

The properties of wool after treatment with the two processes just described, with 2% permonosulfuric acid followed by bisulfite [27] with either 2% potassium permanganate + hypochlorite containing 2% active chlorine [25] or 1% peracetic acid + hypochlorite containing 2% active chlorine [7], are summarized in Table III. All are satisfactory industrial treatments and none of the desirable properties of wool need be lost.

All treated fabrics wet out more rapidly than normal wool, the greatest effect being with the acid bromate–salt chlorination, where the natural water repellency is completely destroyed. Softening agents restore this to a certain extent and make the time of wetting comparable with the other treated fabrics.

Only with permanganate/hypochlorite was any yellowing observed, and this treatment also gave the highest weight loss. However, this was the only treatment to soften the handle, although, except for the chlorination, the other treatments produced no detectable change. There were minor losses in bursting strength (< 10%), the least changed being the acid bromate/salt treated wool. Resistance to abrasion was decreased, the least change occurring with acid bromate/salt and the greatest with permonosulfuric acid.

The treated wools could be dyed evenly with dyes from various classes. Acid bromate/salt had an effect typical of acid chlorination (e.g., [30]) in greatly increasing the rate of dyeing (see Table III for an example). Permanganate/salt and permanganate/hypochlorite increased the rate of dyeing, whereas permonosulfuric acid and peracetic acid/hypochlorite caused a slight decrease. Neutral or alkaline chlorinations also may cause a decreased rate of dyeing [14, 15].

The washfastness of dyes of relatively poor fastness is much lower on acid chlorinated than on normal wool (e.g., [3, 18, 23]); this effect is shown in Table III for Naphthalene Scarlet 4RS on acid bromate/salt treated wool. The fastness is only slightly lower on the other shrinkproofed wools, as is also the case with simple neutral or alkaline chlorinations (e.g., [23]).

The washfastness of dyes of good fastness, such as acid milling, premetallized, or chrome, is either the same or only slightly lower on acid bromate/salt treated wool as on normal wool. The fastness of these fast dyes is the same on wool shrinkproofed by the other oxidation methods as on normal wool.

The combined oxidation-reduction of these shrinkproofing methods can adversely affect many washfast dyes, and it has been found that, even though shade change may be slight, some dyes may wash

**TABLE II. Treatments of Wool with 1.5% Potassium Bromate (on Weight of Wool) in Laboratory Winch Machine**

Liquor:wool ratio 20:1; temperature, 20° C.

| Conc'n $H_2SO_4$, *N* | Conc'n NaCl, *M* | $t_{\frac{1}{2}}$, min. | Area shrinkage, % | Alkali solubility, % | Bursting strength | |
|---|---|---|---|---|---|---|
| | | | | | Conditioned* | Wet |
| (Untreated wool) | | | (40) | (12) | (114) | (86) |
| 0.05 | 5 | 27 | 10 | 15 | 115 | 86 |
| 0.075 | 5 | 14 | 6 | 16 | 114 | 86 |
| 0.10 | 5 | 8 | 5 | 16 | 115 | 86 |
| 0.20 | 5 | 5 | 6 | 16 | 115 | 86 |
| 0.10 | 4 | 15 | 6 | 16 | 115 | 86 |
| 0.10 | 3 | 29 | 8 | 18 | 112 | 85 |
| 1.0 (HCl) | — | 8 | 20 | 20 | 107 | 81 |
| 0.10† | — | 5 | 13 | 18 | 112 | 85 |
| 0.10† | 4 | 6 | 8 | 17 | 113 | 85 |

* 65% RH, 20° C.
† Treatments with 2% active chlorine produced by addition of sodium hypochlorite to the acidified liquor.

**TABLE III. Properties of Wool Shrinkproofed by Oxidation Treatments**

These figures are only relative, being obtained on one fabric; differences have been found with other fabrics, but the results are qualitatively the same for all fabrics tested.

| Property | Untreated wool | Acid bromate/salt, 1.5% potassium bromate on weight of wool | Permanganate/salt, 4% potassium permanganate on weight of wool | Permonosulfuric acid | Permanganate + hypochlorite | Peracetic acid + hypochlorite |
|---|---|---|---|---|---|---|
| Area shrinkage, % | 40 | 6 | 5 | 7 | 5 | 8 |
| Weight increase, % | | −0.6 | −0.3 | 0 | −1.1 | 0.1 |
| Handle | | Harsh* | Unchanged | Unchanged | Softened | Unchanged |
| Reflectance | 46 | 48 | 47 | 46 | 43 | 48 |
| Reflectance after washing 30 min. in 0.05% soap at 50° | | 44 | 44 | 45 | 40 | 45 |
| Bursting strength, conditioned† | 114 | 114 | 108 | 111 | 108 | 110 |
| Bursting strength, wet | 86 | 85 | 81 | 82 | 79 | 82 |
| Bursting strength after washing in 0.05% soap at 50° for: | | | | | | |
| 15 min. conditioned† | 111 | 111 | 103 | 106 | 103 | 106 |
| wet | 85 | 84 | 79 | 80 | 77 | 80 |
| 30 min. conditioned† | 110 | 110 | 101 | 104 | 101 | 104 |
| wet | 85 | 83 | 78 | 78 | 76 | 78 |
| 45 min. conditioned† | 112 | 108 | 100 | 103 | 100 | 102 |
| wet | 86 | 82 | 77 | 77 | 74 | 76 |
| Time of wetting, sec. | 92 | <2* | 27 | 41 | 10 | 21 |
| Rate of dyeing with Naphthalene Scarlet 4RS at 30°, $t_{\frac{1}{2}}$ relative to untreated | 1 | 13 | 2 | 0.8 | 4 | 0.8 |
| Rate of desorption of Naphthalene Scarlet 4RS into 0.05 *M* borate at 40°, $t_{\frac{1}{2}}$ relative to untreated | 1 | 1.9 | 1.2 | 1.2 | 1.2 | 1.2 |
| Alkali solubility, % [21] | 12 | 17 | 18 | 21 | 20 | 20 |
| Soap solubility, % [21] | 1.2 | 2.6 | 2.3 | 2.5 | 3.2 | 2.9 |
| Abrasion resistance, mg. wt. loss for 5000 rubs | 17 | 20 | 26 | 35 | 30 | 22 |

* After wool was softened with Sapamine OC, handle was restored and time of wetting was 35 sec.
† 65% RH, 20° C.

out more easily after shrinkproofing than before. This is due to an effect on the dyes themselves rather than to the shrinkproofing reaction with wool reducing the fastness.

The effect of soap solutions on shrinkproofed wool is of practical importance. It has been shown previously [21] that the wools treated as in Table III lost 1–2% in weight more than untreated wool in a 15-min. test with 0.1% soap solution at 50°, but that the loss in weight during subsequent treatments was similar to that of untreated wool. Yellowing of all the shrinkproofed samples occurred during soap washing, but this was not sufficient to affect the color of fabrics dyed in pastel shades with dyes of adequate fastness. Since white wool should be peroxide bleached for best results, samples of shrinkproofed wools were bleached with 2 vol. hydrogen peroxide at 50° for 2 hr. at pH 9. The reflectance was then 62 (permanganate/hypochlorite was omitted from this test) and after soap washing as in Table III was still 57, that is, much whiter than untreated wool before washing.

Rate of loss of bursting strength of all the shrinkproofed samples was about the same on washing in soap solutions. Direct comparison with untreated wool is difficult, since felting soon increases the bursting strength after an initial decrease (Table III). It appears likely that shrinkproofed wool loses strength at a similar rate to untreated wool. Bleaching causes a 5% decrease in bursting strength of acid bromate/salt treated wool, but the rate of loss of bursting strength in subsequent washing is the same as for shrinkproofed unbleached samples.

*Batch Treatments in Machines other than Winches*

Batch treatments with both the permanganate/salt and acid bromate/salt processes have been successfully carried out in the various machines in common industrial use.

Loose wool, after treatment in a pressure dyeing machine with acid bromate/salt, was manufactured into garments which were satisfactorily shrink resistant. The acid bromate/salt process could not be used with tops in a can dyeing machine, but per-

manganate/salt could be used. Yarn on cheeses or in hanks was successfully treated with both processes in the dyeing machines normally used. Made-up goods such as socks and knitted outerwear may be treated in Smith drum or paddle machines.

*Continuous Padding Treatment of Top*

A problem with continuous treatment in salt solutions is to obtain sufficiently rapid wetting out. Many of the common wetting agents are unsatisfactory; by far the best are solvents such as butanol, butyl cellosolve, or benzyl alcohol (these have been used to increase rates of dyeing [8, 24]). They have the disadvantage of being easily oxidized. In 1% (wt./vol.) potassium bromate/saturated salt in 0.5 *N* acid solutions in the absence of wetting agent, the loss in oxidizing power in 1 hr. at 25° is 9%. If the solution is 0.75% (vol./vol.) in butanol, butyl cellosolve, or Calsolene Oil HS, the losses in oxidizing power are 55%, 28%, and 18% respectively in 1 hr. No satisfactory wetting agents which are oxidized more slowly than Calsolene Oil HS have been found. This is also the best of those studied for continuous permanganate treatments, where butyl cellosolve is oxidized far too rapidly to be of any use. In both treatments, it is desirable to mix wetting agent with the rest of the reagents immediately prior to feeding into the treating bath.

With permanganate/salt continuous treatments, treatment times of 30–60 sec. were found satisfactory using a 6% (wt./vol.) solution of potassium permanganate in 4–5 *M* salt at about 80°. The liquor uptake by wool after squeezing was about 85%. Clearing of $MnO_2$ was simply carried out by passing the wool through a 5–10% (wt./vol.) sodium bisulfite solution for about 30 sec. at 25°. The shrinkages of treated samples of top were 18%, compared with 40% for an untreated sample. There was no change in color and handle of tops due to the treatment.

Acid solutions of chlorine containing high concentrations of sodium chloride have less effect on handle than those without salt. Acid bromate/salt solutions have the following advantages over other chlorination solutions for continuous processing: the theoretical concentration of chlorine is more nearly obtained than when hypochlorite is added to acid solutions with or without salt (85–90% of theoretical compared with 40–60%), color of treated top is superior to that obtained in neutral or alkaline solutions where yellowing is rapid [5], and pH control is far simpler than in neutral or alkaline solutions. The great industrial disadvantage is free chlorine in the atmosphere, which causes corrosion and ventilation problems.

Treatments with acid bromate were in 4 *M* sodium chloride to allow a higher chlorine concentration to be obtained than is possible in saturated salt. Composition of the solution was 0.8% (wt./vol.) potassium bromate, 0.75% (vol./vol.) Calsolene oil HS, and 0.5 *N* acid in 4 *M* sodium chloride. Initial concentration of free chlorine was about 0.7% (wt./vol.), and the top took up about 85% by weight of the liquor. Chlorine was sorbed preferentially by the wool, even though time of immersion was only 5–10 sec. The concentration of chlorine had dropped to about 0.5% after a 2-hr. run during which liquor was replenished with a solution of the above composition. This loss of chlorine was overcome in later runs by having a separate feed of concentrated potassium bromate solution direct to the treating bath, which kept the chlorine concentration close to the initial value.

Tops treated in this way, followed by a 10-sec. treatment in a 1% (wt./vol.) sodium bisulfite solution, two rinsings, a normal backwashing, and two gillings, were whiter but harsher than untreated. Fiber length of treated sliver after combing was the same as untreated. Strengths of yarns made from treated tops were 10–25% greater than similar yarns made from untreated wool, while elongations at break were 15–25% lower.

Knitted fabrics made from treated wool were shrink resistant, but whether they were satisfactorily shrinkproofed or not depended on the knit. Area shrinkages of 5–8% compared with 40% for controls were always obtained on fabrics made from tops which shrank 8–18% for 40% length shrinkage of untreated top. However, some loosely knitted untreated fabrics shrink rapidly in a washing machine and give 40% area shrinkage in only 10–15 min. Treated wool knitted in this way felted on prolonged washing, for example, 16% area shrinkage for 73% on a control in 45 min. in the washing machine. For more tightly knitted fabrics, the untreated of which shrank 30% in 1 hr., treated fabrics shrank from 0 to 3% in 45 min. and only 6–7% in 3 hr. This fabric would be satisfactory from the point of view of the time it would withstand washing as well as by comparison with a control. Better shrinkproofing was obtained (1% area shrinkage on a 73% control for loosely knit

fabric) by passing the top through two acid bromate/salt baths, but the tops were then very harsh.

The handle of treated top, or fabric made from it, can be restored with softening agents. An unexpected result from a study of various softening agents was that several reduced the shrink resistance of the treated top. However, softening had no effect on the shrink resistance of fabric made from shrinkproofed unsoftened wool. Softeners which have an adverse effect (increasing the shrinkage from 15% to 23% for a 40% control) were Catamine, Avistamine A, and Sapamine WL, while those with no effect were Sapamine OC, Avistamine P, Triton X100, and Cirrasol OD. Many others were in between; if tops treated by this method (and perhaps by other methods) were to be softened, the possible loss of shrink resistance would need to be investigated.

## Discussion

Permanganate treatments have the advantage over acid chlorinations of not changing the handle of wool. Permanganate/salt treatments are simpler than permanganate treatments in the absence of salt [28], as the shrink resistance does not need to be developed by the after-reduction, the reducing treatment being almost solely in order to remove precipitated $MnO_2$. In addition, color is better and damage rather less. Permanganate/salt treatments require no analytical control, and conditions of treatment are not important. The given amount of permanganate (4–6% on the weight of wool) is simply allowed to react at a convenient time and temperature, the treatment being complete when the pink color of the liquor has disappeared. Clearing of $MnO_2$ can be done under any desired conditions, this stage being complete as soon as all the $MnO_2$ is removed.

The much higher salt concentration used in the present acid bromate treatment allows faster reaction with lower bromate concentrations and less damage for a given degree of shrink resistance than earlier treatments [16]. The treatment is similar to simple acid chlorinations in its effect on handle, rate of dyeing, and washfastness of dyes, but can be more easily controlled to give even treatments.

The use of a standing bath of saturated salt in each process is a disadvantage, but has raised no problems in mill trials. The presence of such high concentrations of salt is an advantage if too much oxidizing agent is inadvertently added, since wool is protected from the extensive degradation which could take place in the absence of salt. Neither of the above processes requires analyses to be made of reagents or the shrinkproofing liquors. The acid bromate liquor can be simply tested by adding samples to potassium iodide solution and, since the oxidizing power is almost completely lost from the bath during this process, the reaction is complete when little or no yellow color is developed.

Acid chlorinations tend to increase the bursting strength or yarn strength of fabrics. This is probably due to increased fiber frictional coefficients (e.g., [7, 12]) and not to gelatinized material sticking fibers together (e.g., [29]). Strengths of yarn made from treated sliver are higher than those made from untreated wool; this could not be brought about by the sticking together of fibers. Also, the bursting strengths of chlorinated fabrics always remain higher than fabrics treated with other reagents after being washed in soap solutions (Table III) which would be expected to disperse any degraded protein material.

As has been discussed previously, it is difficult to estimate the meaning of laboratory tests on treated fabrics in terms of actual use [20]. The significance of the relatively minor changes of fabric properties (Table III) is unknown, but it is interesting to note that far greater changes with cotton fabrics are accepted (e.g., [9]) and may not be directly related to wearing properties (e.g., [6]). It is unlikely that the changes in properties during shrinkproofing have an adverse effect on the performance of finished goods since, for example, shirts made from acid bromate/salt treated wool have been worn and washed in a machine for 15-min. cycles more than 150 times without deterioration [11].

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# Supercontracting and Setting Behavior of Modified Wool Fibers

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## Abstract

Ultraviolet irradiation of wool fibers increases their rates of supercontraction in unbuffered LiBr solutions and of setting in boiling water. There is a second, slower effect of ultraviolet shown by a progressive reduction in degree of contraction at equilibrium. Treatment with thioglycollic acid or peracetic acid also increases the rates of supercontraction and setting. Iodination or reaction with the Van Slyke reagent reduces the rates. There is little or no loss of tyrosine, and little loss of cystine in the irradiation time which gives the maximum effect on rate of supercontraction. Rate of supercontraction, rate of setting, and second-order transition temperature are closely related properties, as are equilibrium contraction, maximum set, and remanent stress.

## Introduction

Astbury and Woods [3] found that ultraviolet irradiation of wool had the effect of reducing the time necessary to achieve a given degree of set or steam-induced supercontraction. McMahon and Speakman [27], using $M/20$ borax as the setting medium, were unable to detect this, but found that irradiation reduced the degree of set obtained by boiling the fibers in borax solution for 1 hr., followed by release in boiling water for various times.

**TABLE I. Output Energy of 125-Watt Mercury Lamp in Various Spectral Regions**

| Wavelength, Å | Output energy, watts: Line spectra | Output energy, watts: Continuous spectrum |
|---|---|---|
| 2483 | 0.19 | |
| 2576 | 0.27 | |
| 2652 | 0.54 | ~2.3 |
| 2699 | 0.7 | |
| 2753 | 0.12 | |
| 2804 | 0.26 | |
| 2894 | 0.21 | |
| 2967 | 0.36 | ~1.1 |
| 3022 | 0.82 | |
| 3130 | 2.1 | |
| 3342 | 0.24 | ~1.4 |
| 3655 | 3.6 | |

They explained the result in terms of photochemical destruction of cystine disulfide links. Ultraviolet irradiation increases the rate of supercontraction in LiBr solutions, and iodination of the tyrosine residues substantially reduces the second-stage supercontraction rate [20]. These considerations, together with the fact that the apparent activation energy of second-stage contraction in untreated fibers is approximately 30 kcal./mole, led Haly et al. [20] to propose that tyrosine residues are involved in cooperative polar links which help to stabilize the structure of wool keratin.

The problem of how the native structure of proteins is maintained is currently of great interest [8, 12, 14, 24, 26, 32]. In the case of wool it appears reasonable to postulate the existence of cooperating polar bonds, whose stability is partially dependent on coexisting disulfide bridges.

The structure of wool is very sensitive to mild treatment in aqueous LiBr. Hambraeus and Steele [17] found that the $\alpha$-pattern began to disappear when salt concentration was increased to 5 $M$, a concentration too low to cause appreciable supercontraction at room temperature. The pattern returns on removal of salt. When, at higher concentrations and temperature, supercontraction proceeds into the second stage, recovery of the $\alpha$ form is not possible by mere salt removal (see, however, Sikorski [30]). An action of ultraviolet light is to sensitize this irreversible disordering, allowing it to take place under milder conditions. On the other hand, iodination appears to confer stability. The effect is reminiscent of the remarkable $\alpha$ recovery of wool pretreated with Van Slyke's reagent [2]. As will be shown, this recovery is paralleled by extremely slow second-stage supercontraction of similarly treated wool. Increased stability due to various treatments has been noted on a number of occasions [8, 10, 33, 34]; an important role for the tyrosine residue, either through bonding to another residue or through attachment of large groups resulting in steric hindrance, has been suggested. These postulates have been discussed by Crewther and Dowling [9].

In this paper we report the effects on supercontraction and set of ultraviolet irradiation and treatments intended to produce modification either at disulfide links or at tyrosine residues.

## Experimental

Techniques for obtaining supercontraction [18] and set [28] data have been described.

Ultraviolet irradiation was performed using a high-pressure mercury-in-quartz lamp of 125 watts input energy. Output energy at various spectral regions is given in Table I. In all cases the lamp was at a distance of 15 cm. from the fibers. Fibers were rotated during irradiation to ensure uniform treatment.

Thioglycollic acid treatments were in 1 $M$ thioglycollic acid at pH 5 and 37° C. for 3.5 and 21 hr.

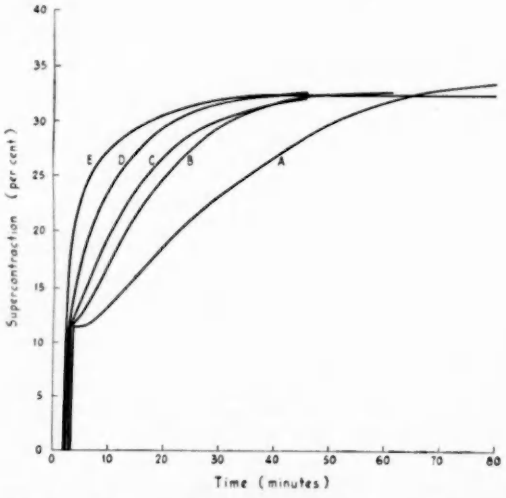


**Fig. 1.** Supercontraction against time curves for wool irradiated by all wavelengths from the lamp. Supercontraction was in 8.1 $M$ LiBr at 100° C. Prior irradiation as follows: (A) no irradiation, (B) irradiated for 2.5 min., (C) irradiated for 5 min., (D) irradiated for 10 min., (E) irradiated for 30 and 60 min.

The corresponding cystine losses were 37% and 53%. Iodination was done following the technique of Richards and Speakman [29] and treatment in Van Slyke's reagent was for 27 hr. at 20° C.

Analysis for tyrosine was by the methods of Goodwin and Morton [15], Bencze and Schmid [5], and by a paper chromatographic method. In the latter, the ninhydrin-developed spot was cut out, heated with more ninhydrin, and the color measured spectrophotometrically against a blank prepared from a piece of paper cut from a place where no amino acids are found.

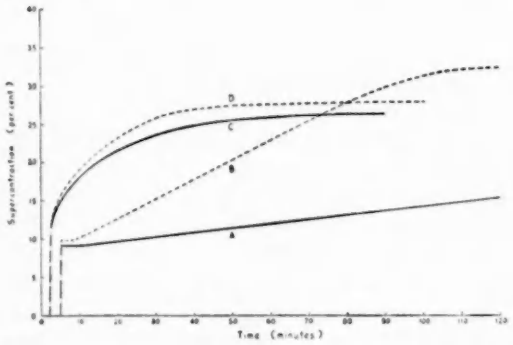


**Fig. 2.** Supercontraction against time curves for wool under the following conditions: (A) no irradiation, 10.4 *M* LiBr at 89° C.; (B) no irradiation, 10.4 *M* LiBr at 100° C.; (C) prior irradiation (all wavelengths from the lamp) for 30 min., 10.4 *M* LiBr at 89° C.; (D) prior irradiation (all wavelengths from the lamp) for 30 min., 10.4 *M* LiBr at 100° C.

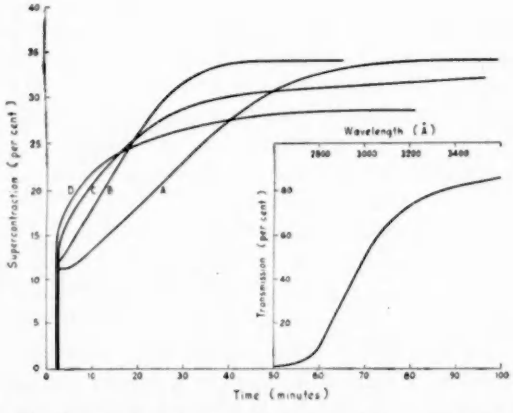


**Fig. 3.** Supercontraction time curves for wool irradiated through filter with low wavelength cut-off at 260 mμ: 8.1 *M* LiBr at 100° C.; (A) no irradiation, (B) irradiated for 1 hr., (C) irradiated for 6 hr., (D) irradiated for 22 hr. Inset shows the transmission curve of the filter.

Three methods of cystine analysis were used; the Shinohara method, the single-fiber method described by Human [22], and the nonhydrolytic method of Leach [25]. The nonhydrolytic method was used for reduced wool, this and the Shinohara method for iodinated wool, and all three methods for ultraviolet irradiated wool.

Except where otherwise stated the wool used was from a pen-fed Corriedale sheep.

## Results

### *Effect of Ultraviolet Irradiation on Supercontraction and Set*

When Corriedale wool fibers were irradiated, the maximum acceleration of rate of supercontraction was achieved in 20–30 min. Supercontraction against time curves for various degrees of irradiation are shown in Figure 1. Here, supercontraction was in unbuffered 8.1 *M* LiBr at 100° C. All the curves of Figure 1 were obtained from about 2 cm. of one fiber. Results for other fibers are similar, but this method was used to eliminate the interfiber variation previously reported [18]. For irradiation times in excess of about 5 min. it is not possible to detect two-stage contraction, and the curves after 30 min. of irradiation indicate a very good approximation to a first-order rate process (*cf.* Haly and Griffith [18]).

Figure 2 shows that the same effect is observed when 10.4 *M* LiBr at 100° C. is used. In the same figure the curves for contraction at 89° C. are given. It appears that increasing the temperature from 89° C. to 100° C. has less effect on irradiated than on unirradiated wool. It is noteworthy that irradiated fibers will supercontract approximately 20% at room temperature, whereas normal fibers will not contract beyond the first stage (here 10–12%) at the same temperature, and indeed only very slowly at 75° C.

The same irradiation treatment of fibers in water, in nitrogen, and *in vacuo* led to similar accelerations of supercontraction rate.

Figures 1 and 2 both suggest that a second effect of ultraviolet irradiation is to decrease the amount of equilibrium supercontraction. Increased irradiation times lead to even lower final contractions. This is exemplified by results (Figure 3) for a fiber irradiated through a filter with a low wavelength cut-off at 260 mμ. (The transmission curve of this filter is shown as an inset to Figure 3.) As irradiation time increases there are a progressive increase

**TABLE II. A Comparison of Rates of Supercontraction and Set for Modified Corriedale Wool Fibers**

| Treatment | 1-hr. index of set | Time for 20% contraction, min. |
|---|---|---|
| Iodination | −9.7 | >100 |
| Van Slyke Reagent | −5.5 | >100 |
| Untreated | 4.0 | 23 |
| Ultraviolet irradiation | 16.4 | ~ 4 |
| Thioglycollic acid (3.5 hr.) | 33.6 | ~ 2 |

in the early rate of supercontraction and a progressive decrease in the final equilibrium value.

When the above filter is used it is not possible to match the supercontraction against time curve which results from 30 min. of unfiltered radiation, apparently because at the wavelengths involved the reduction in equilibrium intervenes; i.e., the change of early contraction rate is produced relatively slowly at the longer wavelengths.

Mitchell and Feughelman [28] found that irradiated fibers gave a higher 1-hr. index[1] of set than normal fibers. It is often true, both in native fibers and in chemically or physically treated fibers, that if one fiber supercontracts faster than another then the 1-hr. index of set will be higher for the former fiber. Some results illustrating this point are presented in Table II. As is shown in Figure 4, the irradiation time necessary to give the maximum effect on set is in good agreement with the time to give the maximum effect on supercontraction; i.e., 20–30 min. of unfiltered radiation.

Despite their higher 1-hr. index of set, the stress which remains in irradiated fibers, held at 40% strain in boiling water for 1 hr. (remanent stress) is higher than the stress retained by normal fibers under the same conditions. The figures are $2.4 \times 10^7$ dynes/cm.$^2$ for irradiated fibers and $1.4 \times 10^7$ dynes/cm.$^2$ for normal fibers from the same sub-sample of wool.

*Cystine Content and Supercontraction of Treated Fibers*

That ultraviolet irradiation causes destruction of wool cystine has been found by a number of workers [4, 16, 31]. Irradiation conditions were different from those in the present study, and therefore cystine analyses were carried out in conjuction with this work. Single fibers were cut into pieces; some pieces were kept for control analyses and some irradiated by wavelengths in excess of 2,900 Å for various times. As reported by Haly et al. [20], the results of two series of experiments indicated a loss of 25–30% cystine in an irradiation time of 1 hr. and little or no further loss due to 100 hr. of irradiation. Subsequently, analyses were done on wool subjected to irradiation by all wavelengths from the lamp. Large inconsistencies were found in results obtained by different operators and by different analytical procedures. All tests indicated, however, that cystine loss in the irradiation time necessary to give the maximum increase of supercontraction rate was no more than 10%. With further destruction of cystine by this method, there is no increase in supercontraction rate.

This result is all the more interesting in view of the fact that treatment of wool with thioglycollic acid greatly accelerates supercontraction rates. Both samples of reduced wool showed extremely rapid contraction, in 8.1 *M* LiBr at 100° C., to a value (34%) in good agreement with normal equilibrium contraction. As usual [18], contraction began just before the fibers were completely penetrated by the reagent and was so rapid that the unpenetrated core could be seen (under the microscope) to be distorted into deep corrugations of amplitude about equal to half their wavelength. As Figure 5 shows, these fibers first contract and then lengthen rather rapidly, approaching a final supercontraction in the LiBr solution of 12%. At room temperature, contraction takes place to the same maximum level, but there is little or no subsequent lengthening. No difference was detected between the two reduced wools in these experiments. Their setting behavior was also alike, 1-hr. indices being 33.6 and 30.8% for the samples which had lost 37 and 53% cystine respectively.

Fibers which had been treated with 1.6% peracetic acid for 1 hr. at 35° C. and then rinsed in aqueous ammonia solution showed similar behavior. Again there was supercontraction (at 100° C.) which was almost instantaneous after penetration of the LiBr solution, and this was followed by extension to a length greater than the natural length of the fiber. The cystine loss due to the peracetic acid treatment is not known, but must have been in excess of 70% [1].

[1] The set retained by a fiber which is held stretched 40% in boiling water for 1 hr., released, and boiled for 1 hr.

*Tyrosine Residues and Supercontraction*

After wool has been treated with the Van Slyke reagent it contracts only very slowly in the second stage. This is shown in Figure 5.

Again, iodination of the tyrosine residues leads to a similar reduction of second-stage supercontraction rate. Figure 6 presents a comparison of supercontraction against time curves of iodinated wool and wool cleaned by the same procedure [29] but not iodinated. Analysis of these wools showed that the cystine content of the iodinated sample was lower than that of the control sample by 18 ± 3%. Thus iodination of the tyrosine residues was not the sole reaction.

Analysis for tyrosine by the methods of Goodwin and Morton [15] and Bencze and Schmid [5] of wool which had been irradiated for 30 min. showed that any loss of tyrosine could not be in excess of 10%. Results were the same for wool irradiated for 30 min. and then heated in 8.9 *M* LiBr for 2 hr. Analysis by the paper chromatographic technique of wool which had been irradiated for 2 hr. also showed no loss of tyrosine in excess of 10%. These results are consistent with those of Graham and Statham [16], who found no loss of tyrosine in wool exposed to long wavelength ultraviolet radiation.

## Discussion

It is clear that ultraviolet irradiation of wool causes a substantial increase in rate of supercontraction in LiBr solutions as well as an increase in rate of setting in boiling water. The irradiation time which gives the maximum effect is only about one-fifth of that necessary to give the maximum effect on dyeing rate [21]. Thioglycollic acid treatment of fibers also causes a very great acceleration of rate of supercontraction and setting, but it is not suggested that the effect is a direct result of disulfide bond breakdown. On the contrary, we have the evidence that the maximum accelerating effect of ultraviolet is accompanied by only a small loss of cystine, longer irradiation times causing more cystine loss but no increase in rate of contraction. In addition, the same final degree of supercontraction can be achieved without loss of cystine [11].

In view of these and other considerations detailed in the *Introduction*, Haly et al. [20] proposed that networks of cooperative polar links help to maintain the native structure of wool keratin, and it is these which are disrupted in the second stage of supercontraction. The stability of the networks is not necessarily independent of the state of wool cystine.

Both ultraviolet irradiation and treatment in thioglycollic acid permit subsequent second-stage contraction at room temperature. If second-stage contraction in a normal fiber requires the rupture of every member of a set of cooperating links, the above effects could be explained by assuming that, after treatment, cooperation is no longer effective, and all links can be considered separately.

Because of the many suggestions made in the literature that tyrosine residues play an important part in protein stability, it is of interest to assess the present evidence with this point of view in mind.

1. Wavelengths in excess of 2900 Å, a region where, in solid keratin, tryptophan is the major absorbing center, although tyrosine and possibly cys-

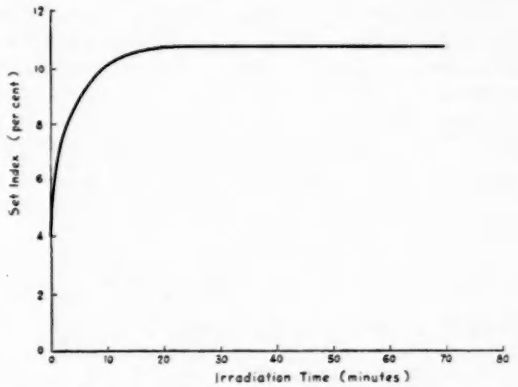


**Fig. 4.** One-hour index of set against time of irradiation pretreatment for Lincoln wool fibers.

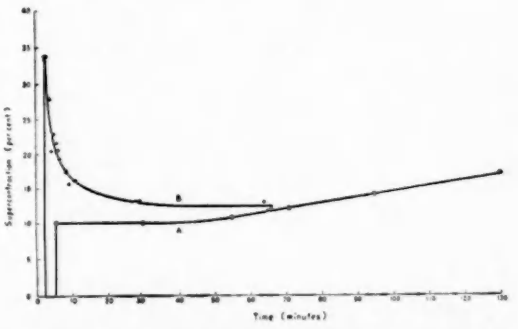


**Fig. 5.** Supercontraction against time curves for (A) fibers previously treated with Van Slyke reagent and (B) fibers previously treated in thioglycollic acid both for 3.5 and 21 hr. Supercontraction was in 8.1 *M* LiBr at 100° C.

tine absorb to some extent [6],[2] have an accelerating effect on rate of supercontraction. No tyrosine is lost during irradiation. One could assume that the excitation energy is transferred from the chromophores and disorders the structure elsewhere, or that an electron involved in a bond at the tyrosine residue is excited to a higher energy level. In the latter case reversibility of the effects of irradiation would be expected, but this has not been observed.

2. About one-tenth of the ultraviolet energy from the mercury lamp, in the spectral region where tyrosine absorbs, is transmitted by the filter with the short wavelength cut-off at 2600 Å. It appears, however, that in 6 hr. of irradiation through this filter the acceleration of rate of supercontraction is less than is obtained in 30 min. of irradiation by all wavelengths from the lamp (Figures 1 and 3). Thus the shorter wavelengths, where phenylalamine, cystine, and probably other groups absorb to some extent, are just as efficient in causing disruption as the wavelengths where the only significant absorption is at the tyrosine and tryptophan residues. This argues against an important role for bonds with tyrosine residues, but not against the concept of a set of cooperating links; we would expect to find many different residues in such a set, and energy absorbed by any of these could help to disrupt the structure.

3. Iodination of wool causes a large reduction in rate of second-stage supercontraction. It is not known whether or not this is a direct result of conversion of tyrosine to di-iodotyrosine. As we have seen, one side effect of the reaction is destruction of 18% of the cystine, and the possibility of other side effects cannot be ruled out. It does seem possible that iodination of tyrosine (or other) residues could, through steric hindrance, make movement of groups, and therefore disruption, more difficult.

4. Treatment of wool with nitrous acid reduces the rate of second-stage supercontraction. The effect may be steric, due to nitrosation of tyrosine or, as suggested by Cadwallader and Smith [8], new cross links may be formed with the tyrosine residue. Other possibilities cannot be eliminated [9]. The full extent of fiber modification is not known, but in any case there is no reason to suppose that tyrosine residues were, before the nitrous acid treatment, involved in a structurally important bond. The mere introduction of bulky groups might produce the effects found whether such a bond existed or not.

In summary, one can say that no evidence forces the assumption that tyrosine residues play a unique part in maintaining the native structure of keratin.

Mention must be made of a mechanism which could explain many of the above results. This is the disulfide interchange reaction [7, 23]. If, during contraction, cystine links break and the "half-cystines" then form new disulfide bridges with other partners, supercontraction could be completely dependent on the amount of cystine and its ability to interchange; there need be no loss of this amino acid. The acceleration of rate of contraction follow-

[2] More recent work has shown that, at wavelengths in excess of 2900 Å, some absorption takes place which cannot be attributed to the above-mentioned amino acids.

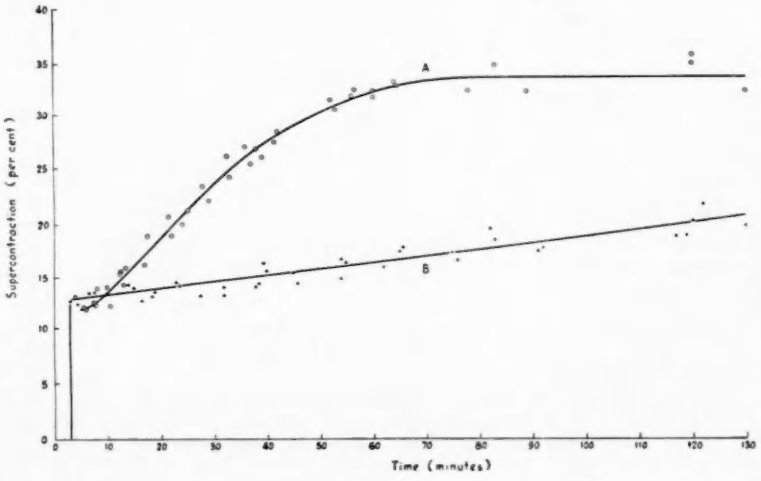


**Fig. 6.** Supercontraction (8.1 M LiBr, 100° C.) against time curves for fibers (A) cleaned by method of Richards and Speakman [29] and (B) cleaned in same way and iodinated.

ing either ultraviolet irradiation or reduction in thioglycollic acid would be explained on the assumption that a small increase in number of sulfydryl groups is sufficient to allow such ready interchange that further production of these groups leads to no increase in rate. It would be necessary to postulate that interchange takes place so rapidly that actual destruction of up to 50% of the cystine causes no increase in rate of contraction beyond that achieved by about 10% loss of cystine. Such assumptions are very powerful indeed, and it seems best to await unequivocal proof that the interchange reaction can proceed to an important extent.

The increase in rates of supercontraction and setting in wool closely corresponds to a reduction of the second-order transition temperature of stretched wool fibers [13]. All these phenomena probably arise from a sensitization to disordering of the polypeptide chains.

Cadwallader and Smith [8] found that ultraviolet irradiation caused disorganization in silk, and this was followed by rebuilding of linkages. It appears that similar events occur in wool. As has been shown, there is a second effect of ultraviolet indicated by a reduction in equilibrium contraction. Because of the long boiling times involved, no check has been made to see if maximum achievable set is reduced by irradiation. However, McMahon and Speakman [27] found that degree of set in *M*/20 borax is so reduced. Unlike Astbury and Woods [3], they did not find any increase in rate of setting but, as they suggest, this is probably due to the fact that setting in borax solution is a very rapid process, and is complete long before the setting time of 1 hr. has elapsed. In addition, the greater remanent stress in an irradiated fiber over that in a normal fiber (both at the same strain) after 1 hr. in boiling water probably indicates a reduced maximum degree of set.

Thus it is likely that reduced equilibrium level of contraction, reduced maximum set, and increase of remanent stress are also closely related properties. Reduction of degree of contraction could result from chain cleavage, since this would mean a shorter average chain length, hence a smaller change on chain randomization [19]. Chain cleavage, however, would not be expected to lead to an increase of remanent stress. The second effect of ultraviolet may therefore be the building up of linkages which are stable to LiBr solutions at 100° C. as well as to boiling of the stretched fiber in water. Reduction of average chain length in this manner would lead to higher remanent stress, since entropic stress depends inversely on chain molecular weight [19]. Finally, the maximum degree of set would be reduced by the same process, both because the restoring stress is higher and because reduced disruption means reduced opportunity for new configurations in stress equilibrium with the extended fiber.

## Acknowledgments

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# An Entropy Stress Study of Various Textile Fibers

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**Abstract**

A stress–strain study has been made of various fibers to determine their entropy force behavior at room temperature. The relative importance of the entropy and internal energy forces is shown with some illustrations of the use of these quantities in understanding the fine structure of polymers. Details are presented to show the effects of extension and godet stretch on some samples.

## Introduction

Many studies of the elastic mechanism of high polymers have been reported in the literature. The majority of such studies have been on rubberlike materials and have, on the whole, been interpreted successfully by the kinetic theory of elasticity. The reader is referred to Kuhn [8], Wall [15], James and Guth [7], Mooney [9], Gee [5], and Treloar [12], to name only a few. However, there has been much less information available on textile fibers where the picture is complicated by large internal forces [1, 2, 4, 6, 10, 11, 13, 14]. This paper presents data for a number of textile fibers and attempts to interpret their behavior in relation to the kinetic theory of elasticity and the known structure of the fiber.

An unoriented fiber consists of a group of crystals or highly bonded regions imbedded in a matrix of more or less free portions of high polymeric chains [6]. As this structure is distorted in a one-dimensional stretch, the general orientation of the molecules, and perhaps also the orientation of the crystals, tends to be in the direction of stretch. This lining-up process encourages crystallization, as it places the molecules in more parallel alignment. If there are appreciable intermolecular forces, the structure will not return to its original random state but will remain in a more or less oriented state. It will, in fact, retract until the entropy or configurational forces are just balanced by the intermolecular or internal energy forces. When a high polymer is distorted, the force developed is composed of two parts: one, due to a change in configuration of the molecule —perhaps an uncoiling—is known as the entropy force; the other, due to a distortion of the bonds or a change in intermolecular forces, is known as an internal energy force. In rubbers, the internal energy force is normally small, and almost the entire force is due to entropy changes [7]. However, in fibers, the internal energy force often is larger than the entropy force. The entropy force is of great interest even though it is a small component,

since it is a clue to the configuration of the molecules within the structure. The basic equation used [7] is shown below.

$$Z = Z_u + Z_s$$
$$= \left(\frac{\partial U}{\partial L}\right)_T + T\left(\frac{\partial Z}{\partial T}\right)_L \qquad (1)$$

Where $Z$ is the total stress, $Z_u$ and $Z_s$ are the internal energy and entropy portions respectively, $U$ is the internal energy, $L$ the relative length, and $T$ the absolute temperature. The entropy force is usually obtained by multiplying the slope of the stress–temperature curve by the absolute temperature. For most of the fibers, the stress–temperature curve is not a straight line, and one must calculate entropy contributions at a given temperature from the slope at that temperature.

Another way of measuring the entropy force is through the measurement of Young's Modulus $E$ and the linear expansion coefficient $\alpha$ of the material. The entropy force may then be calculated from the equation

$$Z_s = -\alpha E T \qquad (2)$$

Since this method is more difficult, it is used only as an independent check of the other method. In this study, emphasis was placed on the configurational changes which occur during a distortion of the sample, rather than on the temperature dependence at a given distortion. All the values given are those obtained at room temperature, and the only temperature changes which were necessary to compute the entropy component of the force were those slightly above and below room temperature.

## Apparatus

A brief description of the apparatus used is included because it was necessary to refine the type of apparatus normally used for testing rubber. A schematic diagram is shown in Figure 1. The specimen clamps and supporting structure are made of invar because of its low thermal expansion coefficient, and even this was corrected by a small piece of stainless steel in order that the distance between the jaws of the clamps (about 2 cm.) would remain constant to within 30 or 40 micro-inches during any temperature change in the range covered. It was also advisable to perforate the invar support in such a manner that it reached temperature equilibrium in about the same time as the clamps. This assured the constancy of the sample length. The sample was extended by means of a synchronous motor coupled to a microscope-focusing rack and pinion. The force-measuring device was a Statham unbonded strain gauge which had a high output, high sensitivity, and motion slight enough to be within the tolerance necessary to avoid disturbing the sample. The temperature of the sample was controlled by a two-bath system; the bath passing over the sample was controlled by a system of solenoid valves. The temperature of the baths was maintained by a heat pump using one bath for the hot side and the other for the cold side, the heat pump being regulated to a definite temperature difference of 40° C. Water was used when some swelling was desired and a 2% NaOH solution was used for greater swelling, especially in the cellulosic fibers. This system worked very nicely in maintaining the constant temperature difference above and below room temperature. For many of the samples tested it was found that, although the total force was quite large, the change in force with temperature was quite small. Since no recorder had both enough sensitivity to read the force difference with temperature and a high enough range to measure the total force, it was convenient to use two recorders, one with a high range to measure the total force involved and the other with a high sensitivity to measure the force–temperature difference. Two Brown Electronik recorders were used—the first with a full-scale sensitivity which could be varied from 50 to 500 g. and the second with a full-scale sensitivity which could be varied from about 2 g. up. These components were controlled by a sequence timer to follow the cycle described below. At the start of the test the sample is given a slight tension at the higher temperature. This tension is recorded on the first

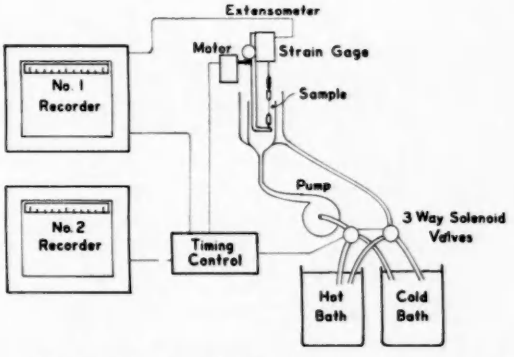


**Fig. 1.** Schematic diagram of the apparatus used.

recorder, and the sample is allowed to relax at constant length for 12 min., leaving a trace on the first recorder. The signal is then switched to the second more sensitive recorder, which measures the differential between the actual signal put out by the strain gauge and the value read on the first recorder. The sample is allowed to continue to relax for one more minute, leaving its trace on the second recorder. The temperature is then changed to the low temperature for 1 min. and returned again to the high temperature for another minute. This then gives a trace on the second recorder which shows the change in force on cooling, and the change in force again on heating, to give a check point. The signal is then returned to the first recorder, the sample is stretched a predetermined amount, say 2%, and relaxation is then continued for another 12 min.; the cycle is then repeated. It has been found that successive stretches on the same sample give more consistent results and do not appreciably differ from the values obtained by taking different samples for every extension.

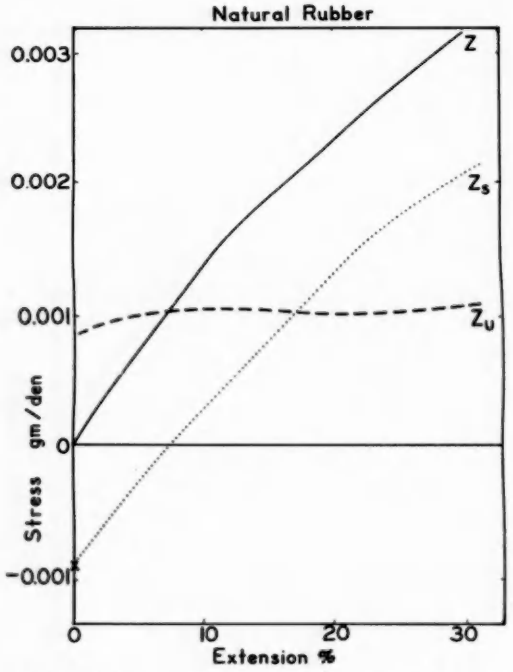


**Fig. 2.** Natural rubber stress–strain curve $Z$, showing its breakdown into entropy $Z_s$ and internal energy $Z_u$ components.

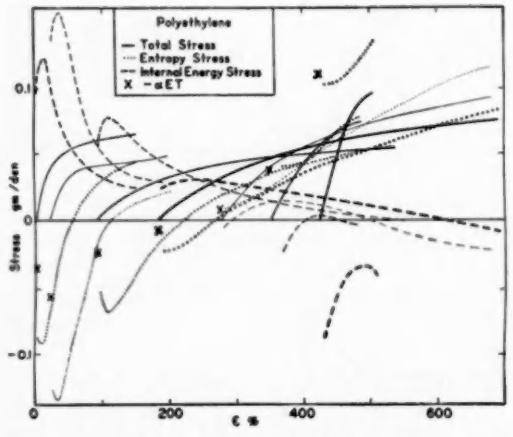


**Fig. 3.** Stress–strain curves and their components for a stretch series of polyethylene samples.

## Experimental Results

### *General*

The wide variation in the physical properties of the various high polymers is striking. For example, the Young's Modulus varies by as much as a thousandfold between different samples. These changes may be divided immediately into two separate groups: those changes due to the difference in chemical composition of the various samples, and those due to physical variation of a given chemical substance. How can these changes be explained? In the relatively simple case of rubber, the observed elastic behavior can be fairly well explained by means of a picture involving chain uncoiling and the addition of an internal pressure or cohesive energy density effect. These effects are described by James

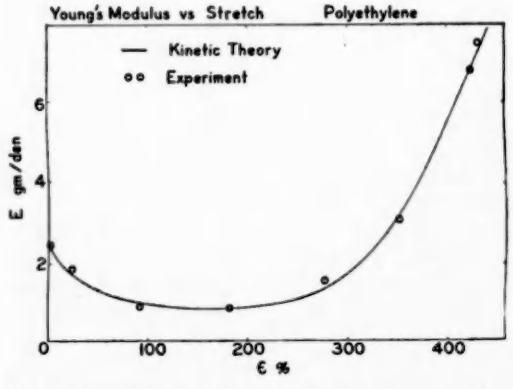


**Fig. 4.** Comparison of theoretical and experimental values of Young's Modulus as a function of stretch.

and Guth [7] in the following equation.

$$Z_s = KT\left[L - \frac{1 + \alpha(T - T_0)}{L^2}\right] \qquad (3)$$

where $KT$ is a measure of internal pressure and $T_0$ is the reference temperature.

The case for most fibers is considerably more complicated. Not only chain untangling or orientation and the internal pressure but also the presence of crystals within the material and the orientation of these crystals must be considered. In general this implies a more predominant role for the internal energy forces, but by no means does this detract from the importance of the entropy forces in determining the structure behavior. This can be illustrated best by discussing the various materials in more detail.

*Rubber*

Rubber is an illustration of one extreme where the molecules are very flexible and the interaction forces very small. This implies that the forces are predominantly entropy-type forces resulting from changes in configuration of the molecules and not influenced appreciably by changes in molecular attraction. This is illustrated in Figure 2, a stress–strain curve of rubber resolved into its entropy and internal energy components. It can be seen from the graph that the internal energy force is almost constant and that in this range of extension the total force changes are due to entropy or configurational changes in the molecule. The cross shown on the graph is the entropy force at zero extension, calculated from Equation 2, using the volume expansion coefficient and the Young's Modulus, and shows excellent agreement with the experimental entropy force measurement. The cohesive energy density of the material can be calculated from the slope of the stress–strain curve and gives the value of about one atmosphere.

*Polyethylene*

The polyethylene molecules are also quite flexible, but they exhibit a higher degree of internal force than rubber molecules and also have a high degree of symmetry. As a result there is a considerable amount of crystallization. Because of crystallization and the higher internal force, polyethylene is not completely reversible at high extension but remains in a stretched state after it is highly extended. A series of samples can be prepared with varying degrees of molecular orientation due to varying amounts of extension. Figure 3 is a composite graph showing the stress–strain curve and resolution into internal energy and entropy components for a series of polyethylene samples prepared by relaxing a highly oriented sample different amounts by varying the temperature of relaxation. All these curves are based on the original unoriented dimensions of the sample. Here it can be seen that the changes in the entropy forces and in the internal energy forces are about the same size, and in fact are considerably larger than the change in the total force. It can also be seen at the higher stretches that the entropy force becomes increasingly more positive and the internal energy force becomes negative.

These general effects are as expected from theory. As the molecular structure is extended, the molecules become more oriented and the entropy force increases to rather large values at the high extensions. The internal energy forces are large at low extensions and at first increase somewhat with extension, then decrease with further extension. A molecular picture may be inferred. Because of the intermolecular forces combined with considerable mobility of the molecules, each molecule has in time adjusted itself through Brownian motion into a preferred position or potential well. An increasing internal energy force is needed to pull the molecules from their potential wells to start molecular orientation. As soon as molecular motion is started, there is a drop in internal energy force, particularly in the direction of stretch. The entropy force in this process shows the inverse behavior. As the molecules are being distorted from their preferred positions, they become more mobile without an appreciable increase in orientation. This causes a decrease in the entropy force. Then, as molecular motion proceeds, the entropy force increases, due to ordering of the molecular network.

The crosses indicate the calculated values of $Z_s$ obtained from Young's Modulus and linear expansion data. These values were measured with the sample under essentially no tension, to eliminate time effects, whereas the usual entropy force measurement requires a certain amount of tension before the measurement can be made. The crosses fit the entropy forces curves rather well at the high stretches and seem to confirm the initial drop in entropy force at the low stretches.

If the values of initial Young's Modulus, obtained from the above polyethylene series, are plotted and

compared with the differential of Equation 3 for an optimum $K$, Figure 4 results. The good agreement between the experimental values and the kinetic theory is quite surprising in view of the observation that the initial portions of the stress–strain curves are influenced to a large extent by internal energy changes. The internal pressure obtained by this method was about 800 atmospheres.

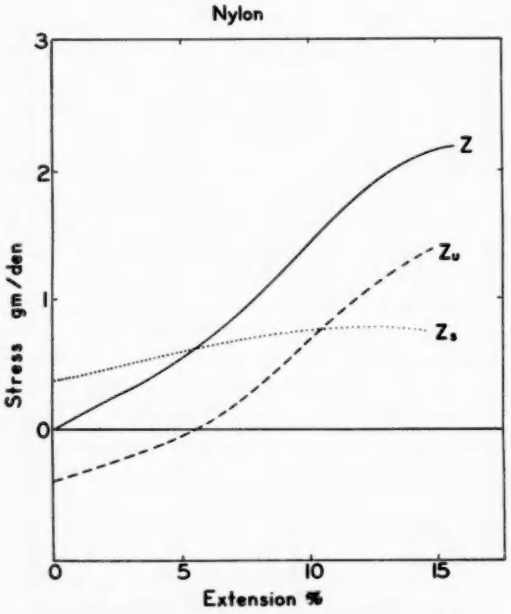


Fig. 5. Typical nylon stress–strain components.

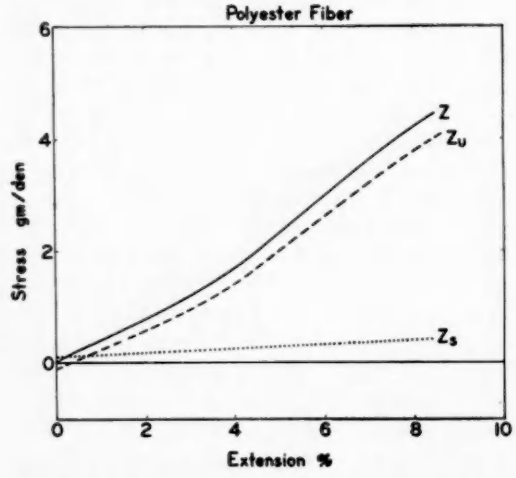


Fig. 6. Typical polyester stress–strain components.

*Synthetic Fibers*

In the case of most of the synthetic fibers, samples have not been available in a wide range of orientations; as a result, a thorough study could not be made. It is hoped that this portion of the general entropy study can be completed when samples become available. However, commercially available samples have been tested and should be typical of the rather highly oriented state. Since the amount of orientation of these samples is unknown, the data presented are based on the dimensions is received rather than on the isotropic state.

A typical nylon stress–strain breakdown is shown in Figure 5. Here it can be seen that the entropy force is positive and increases somewhat with stretch but that the internal energy force accounts for the larger portion of the total force. This might be expected, since the nylon molecule, although rather flexible, has higher bonding energy than the polyethylene. Samples showing even higher bonding energies include a polyester fiber, Figure 6, and finally the acrylic fibers typified in Figure 7. In the last figure it can be seen that the entropy force is

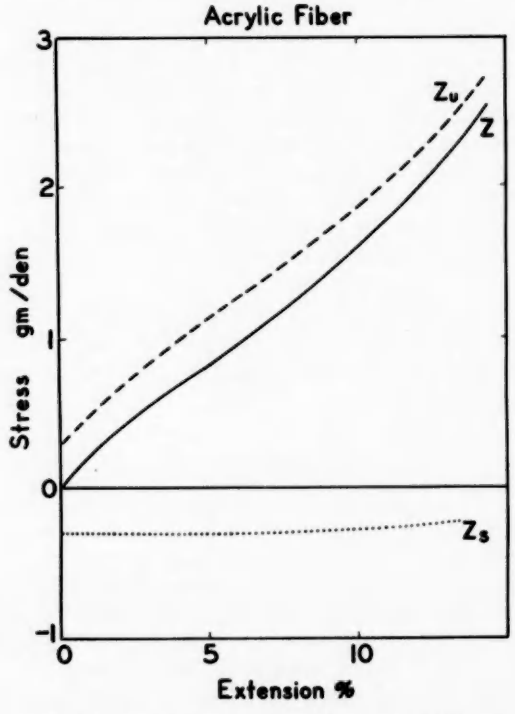


Fig. 7. Typical acrylic stress–strain components.

a small proportion of the total force on the fiber and indeed is negative, even in the oriented state. Its value is found to decrease both when the fiber is crystallized and when it is retracted as in stabilization treatments. This is to be expected, since during both crystallization and retraction the mobile regions are decreasing in length and the molecules are becoming more entangled or unoriented.

The above data were obtained using a nonswelling liquid (ultrasene; a refined kerosene) as a heat exchanger. A considerable increase in the relative contribution of the entropy force can be obtained by using a liquid which causes a certain amount of swelling. This decreases the internal energy force by satisfying the bonds to a certain extent and opens up the network structure by forcing the chains further apart. By the same process the entropy forces are increased as the molecular chains are less restricted by bonds, hence more free to undergo Brownian motion.

*Cellulose Fibers*

The cellulose molecule is a very stiff one having good symmetry and a high ability to attract or bond with its neighboring molecules. This promotes a high degree of crystallinity, and one might expect little if any entropy force. In the dry state this is the case, and the value obtained for $Z_s$ is in the range from $-0.2$ to $-0.6$ g./den. for all samples and does not change appreciably with extension. These values check fairly well with a value of $-0.4$ g./den. calculated for unoriented cellulose using the volume expansion coefficient and Equation 2 and also confirms the value of $-0.36$ g./den. obtained by Roseveare and Poore [11]. The fact that the entropy force changes little with extension and does not seem to depend upon molecular orientation implies that the cellulose chains are so tightly bonded that they are not free to undergo Brownian movement over any appreciable chain segment length. Dry cellulose can then be considered as one extreme in the series, since the forces are almost entirely internal energy forces.

The internal energy forces can be decreased and the entropy forces increased through the use of a swelling agent. The swelling agent, particularly if its molecules are small, tends to satisfy the bonds along the long chain molecule, freeing the chain to a certain extent from its neighbors and allowing the mobility necessary for the entropy force. The measurement of the entropy force in a swelling medium is

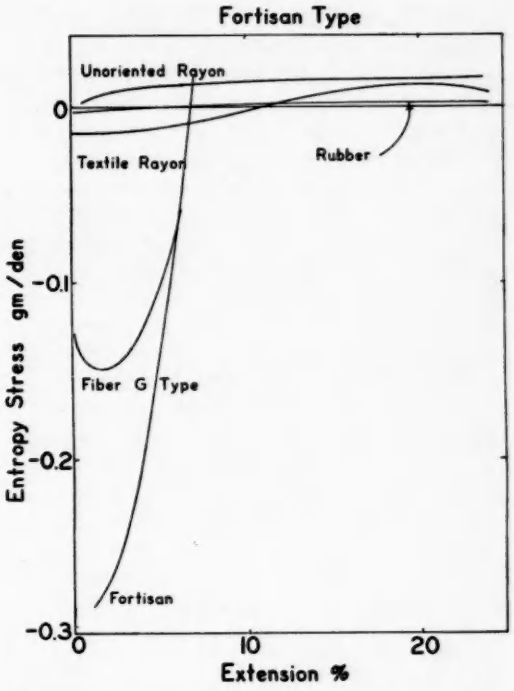


**Fig. 8.** Comparison of the entropy force for various cellulose fibers of the Fortisan type.

open to some criticism, since the degree of swelling may change with temperature and affect the measurement. However, since swelling changes are time dependent, their effects can be minimized by making the temperature change very rapid and extrapolating the stress–time behavior back to zero time. This procedure has proven to be quite satisfactory in almost all cases and also gives a measure of the time dependency found after the temperature change. Passaglia and Koppehele [10] have estimated the effects of swelling on the entropy force measurements over long times. It might be useful to check their technique in correcting for equilibrium swelling against the above extrapolation.

In order to observe the effects of swelling in cellulose, two swelling agents were used: water and 2% NaOH solution. The data taken on regenerated cellulose samples show that there are two general types, depending on the method of manufacture. The first type to be considered might be called the Fortisan type, since Fortisan illustrates the highly oriented extreme. Figure 8 illustrates the entropy forces obtained in water. The rubber curve is in-

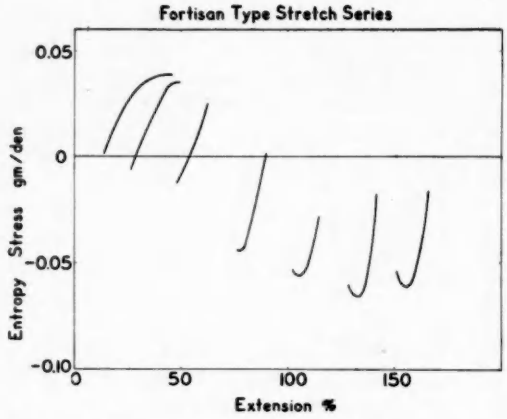


Fig. 9. Entropy force curves for a Fortisan type stretch series.

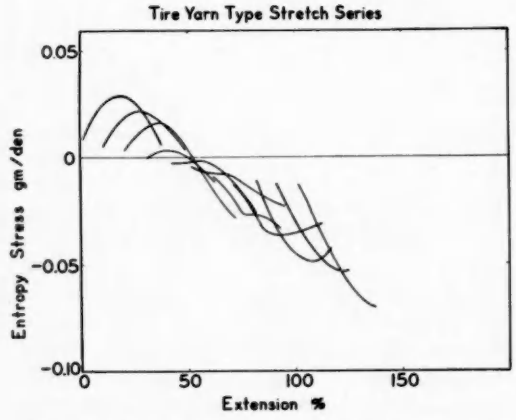


Fig. 10. Entropy force curves for a tire yarn type stretch series.

cluded only to illustrate the comparative magnitude of the forces. Quite apparent from this figure is the fact that at low extensions the entropy force is progressively lower as the original orientation of the sample increases; i.e., the unoriented cellulose has the highest value. This behavior is opposite to that found in polyethylene, nylon, etc. It will also be noticed that the more highly oriented the sample, the greater is the slope of the entropy curve.

Another way of presenting these data in a graphic manner is to assume an equivalence between godet stretch and sample extension and plot the curves as was done in Figure 3 for polyethylene. For cellulose this is not a rigorous procedure, since godet stretch is not exactly equivalent to extension of the

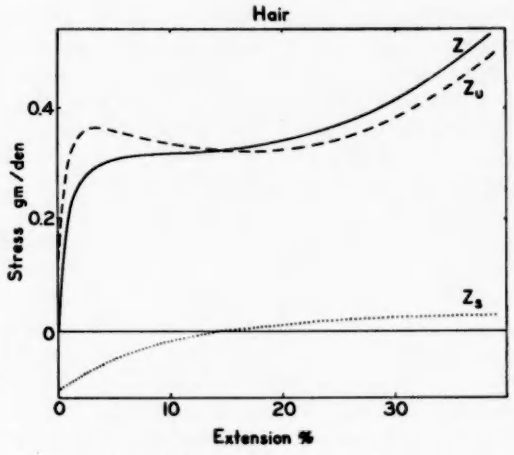


Fig. 11. Typical hair fiber stress–strain components.

final sample, and a 0% godet stretch sample is far from isotropic. However, such a graph is helpful in visualizing the changes occurring with orientation in a qualitative way. Such a plot is shown in Figure 9 for a Fortisan type stretch series. The extension and stress are based on the dimensions of a 0% godet stretch sample. This series demonstrates the general downward trend of the family of curves and also the increasing slope of the separate curves as the godet stretch is increased.

The other type of regenerated cellulose behavior is shown by tire yarns in Figure 10. Here again, the family of curves tends to go down with increasing stretch. However, the individual curves assume a more and more negative slope as the godet stretch is increased.

There are two main reasons why the entropy force may decrease: either there is a configurational change decreasing the orientation of the molecules in the mobile regions or there is a decrease in mobility of these molecules due to higher internal energy forces (chemical or steric), greater chain stiffness, smaller chain length between fixed points, etc.

The methods of manufacture suggest a possible interpretation of the above data. The F type yarns are made in such a way that before the cellulose structure is set or condensed the godet stretch is performed and at this time the molecular chains are in a swollen state and very free to readjust themselves. Thus, tangling is kept to a minimum and crystallization is encouraged. This means that crystals grow large and are a large proportion of the

total cellulose. At low godet stretch the molecular chains are nearly randomly oriented and in a fairly stable state, and the fact that they are mobile makes little difference. However, at high godet stretch the chains are nearly parallelized and, because they are mobile, they rotate and readjust themselves into a rather good crystalline array. The yarn then is allowed to relax in order to avoid brittleness. This means that those regions which did not crystallize are allowed to randomize as much as they can, aided by the fact that these regions have been crowded and distorted by the crystal growth. Although this relaxation may be only a few percent of the total fiber length, it causes a pronounced randomization of the noncrystalline regions, as the crystals do not relax to any great degree. This also implies that a few percent extension of these samples should orient these regions again, as shown by the rapid increase in entropy force of the individual curves. This forms a clear and consistent picture of the F type yarn, explaining the low initial entropy force for highly oriented samples and its rapid increase with extension. How then can the observed data on tire yarn be explained when it shows behavior almost opposite to that of the F type yarn? Perhaps a clue toward an understanding is again to be found in the method of manufacture. Tire yarns are made in such a way that at the time the liquid viscose is set up, cross links are formed by the zinc ions between xanthate groups. This action immobilizes the cellulose chains to a great extent and does not allow individual chain freedom. The structure is not so highly cross-linked that it cannot be highly oriented by stretching, but the individual chains are not free to rotate or readjust to any great extent. Thus, crystallization is greatly inhibited, and the crystals that do form are probably small and rather imperfect and involve a smaller proportion of the cellulose than in the F type yarn.

Here again the entropy force decreases with godet stretch, implying either an increase in interchain forces in the mobile regions or a decrease in orientation of these regions. At low godet stretch the curves look much like those of the Fortisan type, as might be expected, since the zinc cross-linking mechanism is not effective at zero godet stretch. However, at higher godet stretch the $Z_s$ vs. extension curves show a behavior opposite to the Fortisan type, as they show a marked decrease in the entropy force on extension. It is not very reasonable to conclude that orientation is decreasing, particularly since the curve is reversible. Thus, it must be concluded that the intermolecular forces increase with extension and therefore decrease the mobility of the molecular chains in the mobile regions. This is not unreasonable if these regions are considered to be rather well oriented but also tangled. Stretching would then cause the chains to come closer to each other and increase both bonding and steric forces.

Perhaps another way of stating it is to say that in the Fortisan yarn the crystals are large and relatively perfect and the amorphous regions are small and quite amorphous. That is, the order within the fiber varies from high to low. However, the tire yarn type shows small imperfect crystals and large but not very free amorphous regions. That is, the order within the fiber shows much smaller variation.

If a higher degree of swelling is induced by the use of 2% caustic solution, there is an increase in the entropy force, especially in the more highly oriented samples, as would be expected. In some cases the yarns tend to shrink on swelling, demonstrating the increase in entropy force. There is a pronounced increase in the slope of the individual entropy force curves, especially in the highly stretched tire yarns. This again is consistent with an increase in molecular mobility. It would be interesting to carry out experiments at greater degrees of swelling; perhaps this may be done in the future. These results are in contradiction with those of Roseveare and Poore [11], who report no change in the slope of the stress–temperature curve with swelling in 3% or 4% NaOH.

The natural cellulose fibers presented a number of experimental difficulties. There is a great deal of variation from fiber to fiber, which necessitates many measurements in order to obtain a representative average. The low degree of swelling also means a large Young's Modulus and low extensibility. This is particularly true of the bast fibers. These fibers show a definite increase in entropy force with increased swelling. However, the entropy force is either constant or decreases somewhat with stretch. Cotton shows a definite decrease in entropy force with stretch, rather similar to tire yarn.

Cellulose acetate shows an entropy force behavior very similar to a Fortisan type cellulose but slightly higher, going into positive values on stretching a few percent. This behavior is expected, as there is no cross-linking during manufacture, and the acetyl

groups present along the cellulose chain inhibit crystallization and act in much the same manner as a swelling agent in allowing more freedom in the molecular chains. However, the major difference between the forces developed in cellulose and acetate is in the internal energy.

*Protein Fibers*

A few protein fibers were tested and will be mentioned briefly here. However, no attempt was made to study this general class of fibers in detail [8]. In the dry state, silk shows a large internal energy force and a negative entropy force which changes little with stretch. In the wet state, however, the entropy force is positive and increases considerably with stretch. This implies that the molecules are rather well oriented in the mobile regions, much as x-ray evidence indicates that they also are oriented in the crystalline regions.

As a representative of the regenerated protein fibers, a Zein yarn was studied. In the dry state, the behavior was similar to silk, although the forces were considerably smaller. In the wet state, however, the entropy force had a small negative value and did not change on stretching. In a 2% caustic solution, the entropy force assumed a small positive value and accounted for almost the total force (the internal energy force having dropped practically to zero). The entropy force also showed a large amount of secondary bonding, which inhibited the freedom of the molecules at low swelling but was broken at high swelling. However, in the highly swollen state there did not seem to be any primary cross-linking bonds to hold the molecular network together.

The hair fibers showed an interesting behavior, as seen in Figure 11 and as previously measured by Bull [3]. Here the entropy force is quite normal in its general behavior, but the internal energy force shows a maximum near the knee of the stress–strain curve. This is interesting in view of the folded-chain theory of molecular structure. However, although this behavior is consistent with a folded-chain structure, it is by no means a proof thereof, since the same general behavior was found in some polyethylene samples (see Figure 3).

## Summary

The entropy forces developed on extension are compared for various textile fibers as measured at room temperature. The samples can be listed in decreasing ratio of entropy forces to internal energy forces as follows: rubber, polyethylene, nylon, polyester, acrylic, and cellulose. This also shows the order of increasing internal pressure. The variation of entropy force with extension is used as an indication of the morphology of the fiber. This technique is shown to be especially useful when applied to a series of samples of different orientations. Three such series are presented—one polyethylene and two different types of cellulose. There is some discussion of the effect of swelling on these variables.

## Acknowledgment

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# Correlation between Colorfastness and Structure of Anthraquinone Blue Disperse Dyes

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**Abstract**

A correlation is established between the structure of blue amino anthraquinone dyes for cellulose acetate, cellulose triacetate, and the polyester fibers and the colorfastness they exhibit towards the atmospheric agents responsible for gas and ozone fading and towards the action of light. Any structural modification which reduces the electron density on the amino nitrogen attached to the anthraquinone ring, whether it is an amino, an alkylamino, or an arylamino nitrogen, will increase the resistance of the molecule to the electrophilic agents responsible for the chemical changes which occur during fading. Several anthraquinone structures with improved resistance to fading are reported. These contain, as substituents on the arylamino radical, groups which withdraw electrons from the aromatic ring, leaving the amino nitrogen with a low electron density.

## Introduction

Disperse blue dyes which are derivatives of anthraquinone have long been used on acetate fibers; recently this use has been extended to include the dyeing of both triacetate and polyester fibers. The vulnerability to atmospheric fading of these compounds on acetate has led to an intensive search for blue anthraquinone structures that would resist this change. Gas fading is the term applied to the reddening that occurs when fabrics dyed with certain of the blue anthraquinones are exposed in service to atmospheres contaminated with industrial wastes. It has been shown [5, 7, 11] that nitrogen dioxide is the active agent causing degradation of the dye under these conditions. Extensive investigation has established that certain of the amino anthraquinone derivatives are much more resistant to the action of nitrogen dioxide than are the simple 1,4-bis(alkylamino) anthraquinones. The substitution of an arylamino group for an alkylamino group greatly enhances the resistance to gas fading, as does the replacement of a free amino by an hydroxyl group [10]. The effect upon gas fading of such structural changes is given in Table I.

It has been shown recently that, in addition to nitrogen dioxide, there is frequently sufficient ozone present in the atmosphere to react with vulnerable amino anthraquinone dyes and to cause a bleaching out of the blue color [9]. The sensitivity of several anthraquinone derivatives to the action of ozone is included in Table I. These results show that those structures which are more resistant towards nitrogen dioxide are also more resistant towards ozone (O) fading.

The amino anthraquinone blues have been found to have excellent affinity for the various polyester fibers. However, the simple 1,4-bis(alkylamino) derivatives show a very low level of lightfastness on these fibers. This is different from the behavior shown on acetate, where the level of lightfastness of these anthraquinone blues is generally satisfactory. Evidently the substrate plays a role in this degradation. However, here, too, the extent to which the reaction occurs depends upon the presence or absence of specific structures. As shown in Table I, those structures which are more resistant towards gas fading and O fading on acetate are also more resistant towards the effect of light on the polyester fibers. Careful analysis of the colorfastness properties of a large number of amino anthraquinone derivatives has made it possible to establish definite relationships between fading and structure. The present work attempts to explain these relationships in terms of modern electronic concepts, with the added objective of facilitating the formulation of other resistant structures.

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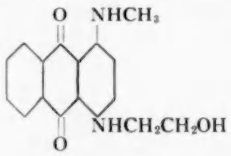
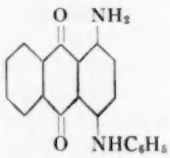
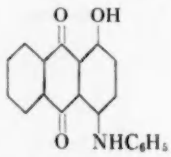
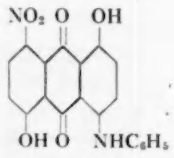
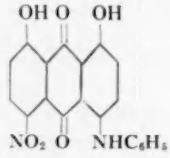
## Experimental

As shown in Table I, the most resistant anthraquinone structures are those containing the 1-hydroxy-4-arylamino configuration. There are two major homologous series which are based on this fundamental structure: the derivatives of 1,5-dihydroxy-4-arylamino-8-nitro anthraquinone and of the isomeric 1,8-dihydroxy-4-arylamino-5-nitro anthraquinone [2, 8], most of which are blue; and the derivatives of 1-hydroxy-4-arylamino anthraquinone [6], which are purple rather than blue. Although the parent member of each of these series has a high level of resistance to gas fading, there are distinct variations within each series which range from a very low level of colorfastness to a very high one. It was found that these variations could be attributed directly to the constitution of the arylamino group in position 4. For example, acetate

**TABLE I. Improved Colorfastness Due to the 1-Hydroxy-4-Arylamino Configuration**

| Structure | Gas fading change on acetate after 1 AATCC unit* | Gas fading change on acetate after 4–5 AATCC units | O fading change on acetate after 16 hr. in ozonizer† | Light change on Dacron‡ after 40 hr. in Fadeometer |
|---|---|---|---|---|
|  | 2 | 0–1 | 1 | 1 |
|  | 3 | 1 | 1 | 2 |
|  | 5 | 4 | 3 | 4 |
|  | 5 | 4 | 3 | 4 |
|  | 5 | 4 | 3 | 4 |

Code: 5—no change, 4—slight change, 3—moderate change, 2—marked change, 1—severe change.

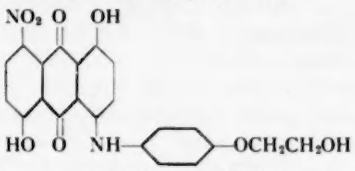
* Dyed fabrics were exposed in the AATCC test chamber for gas fading; 0.25% dyeings were tested. One unit is the time required to fade the AATCC Control Sample to the redness of the vat-dyed Standard of Fading; three units is three times this exposure, etc.

† Fabrics dyed as above were exposed in the laboratory ozonizer. Details of this are given [9].

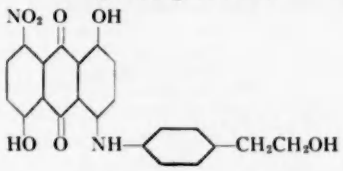
‡ DuPont trademark.

fabric dyed with 1,5-dihydroxy-4-*p*-hydroxyethoxyphenylamino-8-nitro anthraquinone exhibits a marked reddening after 1 AATCC unit of gas fading (defined in Table I), whereas 1,5-dihydroxy-4-*p*-hydroxyethylphenylamino-8-nitro anthraquinone produces fabric that shows only a slight change after 5 units of gas fading.

Marked change at 1 unit

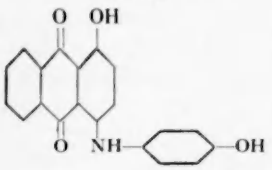


Slight change at 5 units

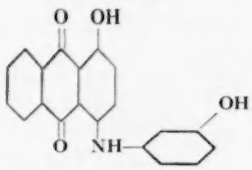


These same differences are found in the other homologous series: 1-hydroxy-4-*p*-hydroxyphenylamino anthraquinone reddens markedly after 1 AATCC unit of gas fading, whereas 3 units of fading are needed before the corresponding *m*-hydroxyphenylamino derivative reaches the same degree of reddening, and even after 5 units of fading, the phenylamino analog shows only a slight change in shade.

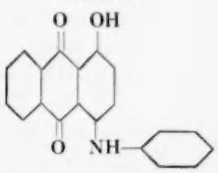
Marked change at 1 unit



Marked change at 3 units



Slight change at 5 units



The same order of sensitivity is found when these compounds are tested for O fading on acetate fibers and for lightfastness on polyester fibers.

The various members of these homologous series can be synthesized by condensing the appropriate aniline derivative in a suitable solvent with the properly constituted anthraquinone [10]. Thus a large number of these derivatives have been synthesized and very carefully evaluated for resistance towards gas fading. In Table II the amines used in these condensations have been classified according to the effect they have upon the gasfastness of the resulting arylamino anthraquinone. The amines listed in Columns 1 and 2 are those which form anthraquinone derivatives with the lowest resistance towards gas fading. For example, the amines in Column 2 produce dyes which fade markedly after 1 AATCC unit of gas fading as described above for the derivative made from *p*-hydroxyethoxy aniline. The amines listed in Columns 4 and 5 are those which form derivatives which are the most resistant to gas fading. For example, the dye made with *p*-hydroxyethyl aniline shows only a slight change after 5 AATCC units of gas fading, and that made from aniline can be considered as showing almost no change. With but a few minor exceptions the relative positions of the amines is the same for both homologous series.

## Theoretical Considerations

Close examination of Table II reveals several rather fundamental relationships between structure and behavior.

A *p*-alkyl aniline forms an anthraquinone derivative that is much more resistant to gas fading than is the analogous derivative made from a *p*-alkoxy aniline. The introduction of an hydroxyl group on the alkyl or alkoxy chain does not significantly alter this relationship.

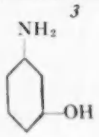
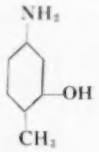
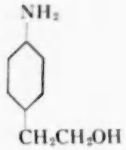
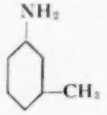
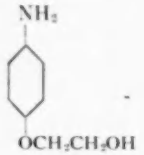
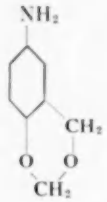
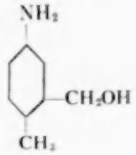
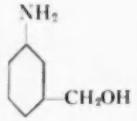
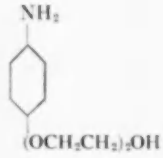
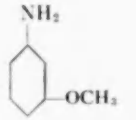
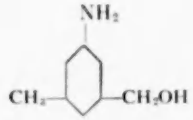
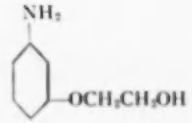
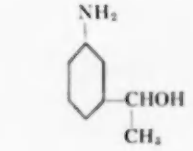
The gasfastness of the derivative made from a *m*-alkoxy aniline is far superior to that made from the corresponding para isomer. This applies to all —OR substituents (R = H, alkyl, or hydroxyalkyl). This large difference between the meta and para isomers is not found with the alkyl derivatives.

Thus both the nature and the position of the substituent on the arylamino radical in these anthraquinone structures determines the gas fading properties of the entire molecule. An understanding of the fundamental reasons for these relationships can be obtained by considering the effect of the various ring substituents on the electronic configuration of the arylamino group. A great deal of information is

available concerning the effect of ring substituents upon the basicity of many derivatives of aniline. Basicity is related directly to electron density; the greater the electron density on the amino nitrogen, the more basic it is. The conclusions that have been obtained for aniline and its derivatives should also be applicable to the arylamino group that is attached to the anthraquinone nucleus in these dyes.

The over-all electronic structure of an aromatic compound depends upon both the mesomeric and the inductive effects exerted by the substituents on the aromatic ring. However, each substituent can be considered in terms of whether the main effect is that of donating electrons to the ring or of withdrawing them from the ring. In each instance the molecule achieves a permanent polarization, and it is this redistribution of charge that determines the chemical properties. When an atom containing an unshared pair of electrons such as is found in an —OR group (R = H or alkyl) is attached to an aromatic ring, the unshared pair of electrons enters into a bond, with the ring carbon causing electromeric disturbances which increase the electron density at the ring positions ortho and para to the —OR substituent. In view of the increase in electron density, such groups can be considered as donating

**TABLE II. Amines Used to Synthesize 1,5-Dihydroxy-4-Arylamino-8-Nitro Anthraquinone; How They Affect Gasfastness**

| Forms a dye very sensitive to gas fading | | Forms a dye moderately resistant to gas fading | Forms a dye very resistant to gas fading | |
|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* |
| | |  | | |
| | |  |  |  |
| |  |  |  |  |
| |  | |  |  |
| | | |  |  |

electrons. Thus, if there should be an amino group para to an —OR, there will be an increase in the electron density on the amino nitrogen. For example, *p*-hydroxy aniline is considerably more basic than aniline itself. According to this, the arylamino nitrogen in 1,5-dihydroxy-4-*p*-hydroxyphenyl-8-nitro anthraquinone would be considerably more nucleophilic than the arylamino nitrogen in the corresponding unsubstituted anilino derivative. When the —OR group is meta to the amino group, this increase in electron density occurs on the position adjacent to the amino nitrogen rather than on it. Therefore, *m*-hydroxy aniline is a much weaker base than *p*-hydroxy aniline, being only slightly more basic than aniline itself. The electromeric changes that occur when an aromatic ring contains an alkyl substituent are such as to cause only a slight increase in the electron density in the ortho and para positions. Consequently the basicity of *p*-toluidine is only slightly greater than that of aniline and of *m*-toluidine and is very much less than that of *p*-anisidine. Re-examination of Table II in the light of these observations shows that the structural changes which cause an arylamino group to form a dye with a high level of resistance to gas fading are the same ones which cause a derivative of aniline to have a low level of basicity. These data all indicate that a high electron density around the arylamino nitrogen renders the anthraquinone molecule more subject to attack by the nitrogen dioxide active in gas fading.

There is more direct experimental evidence which shows that the dye structures which resist gas fading do actually have a lower electron density on the arylamino nitrogen. As stated above, basicity and electron density are directly related. By means of a potentiometric titration in glacial acetic acid it has been possible to determine the $pK$ values for certain of these dyes. 1,4-bis(methylamino) anthraquinone, which is one of the dyes most subject to gas fading, has a $pK$ value of 4.75, whereas 1-hydroxy-4-phenylamino anthraquinone, a relatively resistant structure, has a $pK$ value of about 0.35. These results show that there is a definite correlation between gas fading and the basicity of the anthraquinone derivative. The degree of basicity in a compound such as 1-hydroxy-4-phenylamino anthraquinone can arise only from the electron density at the arylamino nitrogen.

There is also circumstantial evidence which favors the above concepts by emphasizing the importance to the whole dye molecule of the mesomeric effects within the arylamino group. This circumstantial evidence can be found in the slight differences in shade that are found among the analogs of a given dye series. For example, when 1,5-dinitroanthrarufin is condensed with either *p*-hydroxy aniline, *p*-anisidine, or *p*-phenetidine, the resulting dyes are significantly greener in tone than those made from the corresponding meta isomers. The greenness of shade indicates the presence of additional resonance forms in the para-substituted analogs as compared to the meta. The mesomeric effect favors the formation of quinoidal structures in the para isomers that cannot be formed in the meta isomers. These additional quinoidal structures contribute to a greater electron mobility and thus produce the more hypsochromic, greener shade. Therefore, presumably, the greenness indicates that the mesomeric effect is a strong one, producing quinoidal structures and concurrently increasing the electron density on the arylamino nitrogen.

Once the aromatic amine has been condensed with the anthraquinone nucleus, the arylamino nitrogen must be considered in relation to the rest of the molecule as well as to the benzene ring. Thus the nitrogen atom is also under the influence of the hydroxy group which is para to it on the anthraquinone nucleus and which will tend to increase the electron density on it. The final electron distribution depends upon all the various factors that are at work within the molecule, and it may be that the substituents on the benzene ring have to function in such a way as to absorb or decrease the charge that accumulates on the nitrogen from the anthraquinone ring. All this produces a rather complex picture; one that is as yet incompletely understood. Apparently, however, on the basis of the above observations, it is possible to obtain an idea of the end result by merely considering the arylamino radical and its substituents. Any configuration of this group that tends to decrease the electron density around the arylamino nitrogen will also decrease the sensitivity to gas fading.

### Chemical Characteristics of the Fading Reactions

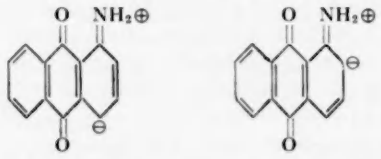
The concept that an anthraquinone structure containing a strongly nucleophilic nitrogen atom enters into the reaction with nitrogen dioxide more readily than does one containing a less nucleophilic nitrogen

atom fits in with the current ideas on the chemical nature of the gas fading reaction. Nitrogen dioxide from the atmosphere is believed to be the primary causative agent [11], with oxygen and perhaps other oxides of nitrogen playing an undetermined role. All of these are electrophilic agents needing a high degree of negativity at the point of attack. Diazotization of a primary amino group, nitrosation of a secondary amino group, and oxidation have been proposed as possible mechanisms for the reaction between nitrogen dioxide and the various alkylamino anthraquinones [5, 7]. More recently, Couper isolated a number of degradation products formed by the gas fading of 1,4-bis(methylamino) anthraquinone [1]. The structure of these products emphasized the role played by oxidation and indicated other reactions such as dealkylation and deamination. Regardless of the exact mechanism, it has been shown that the gas fading reaction is the result of the attack of an electrophilic agent upon the alkyl- or arylamino nitrogen which consequently must be a center of high electron density, i.e., a strong nucleophile. Therefore, any means of reducing the degree of negativity on the vulnerable nitrogen will reduce the extent of the gas fading reaction.

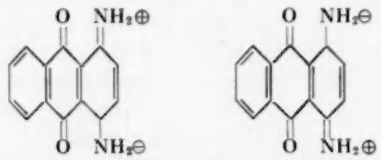
This group of amino anthraquinone dyes is also subject to attack by ozone, as evidenced by O fading [9]. Ozone is an even stronger electrophilic agent than nitrogen dioxide. Therefore, any structural change which reduces the nucleophilic character of the amino nitrogen should also reduce the degree to which these dyes are destroyed by ozone. This was found to be the case. Those anthraquinone structures which show increased resistance towards gas fading because of a reduction of the electron density on the amino nitrogen also show increased resistance towards O fading and, in addition, they have a superior level of lightfastness when dyed on polyester fibers. The latter observation indicates that the active agent in the degradation due to light may also be electrophilic in nature and gives support to the idea expressed by Egerton [3] that the formation of hydrogen peroxide is an important part of the fading reaction due to light.

## Additional Applications

The concept that reduced electron density on the amino nitrogen causes an increased resistance to gas fading can be utilized to explain what has long been considered an anomaly in the gas fading behavior of the anthraquinone dyes. 1-Amino anthraquinone is relatively resistant to gas fading, whereas 1,4-diamino anthraquinone exhibits a marked change after exposure to only 1 AATCC unit of gas fading. Consideration of the many possible resonance forms of 1-amino anthraquinone reveals two which are of particular interest in the light of the present discussion:

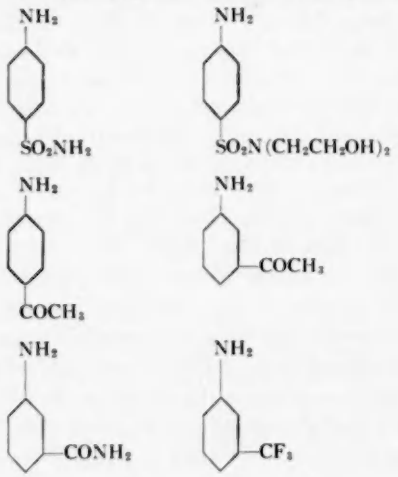


Both of these forms are such as to greatly reduce the nucleophilic character of the amino nitrogen and to render it less susceptible to attack by nitrogen dioxide. On the other hand, the significant resonance forms for 1-4 diamino anthraquinone are:



Such resonance serves to effectively divide the charge between the two amino groups, thus producing two nitrogen atoms each with a sufficiently high

**TABLE III. Aniline Derivatives with Electronegative Substituents which Form Colorfast Derivatives of 1,5(1,8)-Dihydroxy-4-Arylamino-8(5)-Nitro Anthraquinone**



electron density to be readily susceptible to attack by an electrophilic reagent. Therefore, this structure shows a greater degree of gas fading than does the 1-amino anthraquinone.

Among the many anthraquinone blues, there is one other important type of structural change that has produced dyes with improved resistance to gas fading. The introduction of a strong electronegative group such as —CN on the anthraquinone nucleus in the position ortho to the amino group [10] greatly enhances the gasfastness of the compound. In terms of electronic structure such a group reduces the electron density on the amino nitrogen while causing a charge redistribution in the rest of the molecule. Thus, in these somewhat different structures, the important factor is once again the electron density on the amino nitrogen.

## Formulation of New Dye Structures

Consideration of the various ways to reduce the electron density on the amino nitrogen led to the formulation of some new dye structures which would be expected to have excellent resistance to gas fading. When groups such as $—NO_2$, —COOH, —CN, $—COCH_3$, and $—SO_2R$ are attached to an aromatic ring they tend to withdraw a charge from the ring. This withdrawal involves mainly the $\pi$-electron density and takes place preferentially, leaving the greatest deficit in the ortho and para positions. The presence of a nitro group in the para position of the arylamino substituent on the anthraquinone nucleus would reduce the electron density on the arylamino nitrogen well below the level occurring in the simple anilino derivative, thus forming a more resistant dye. However, it is difficult to synthesize an arylamino derivative of 1,5-dinitroanthrarufin or 1,8-dinitrochrysazin in which there is such an electronegative substituent on the arylamino group. If the basicity of the amino nitrogen is reduced to too great a degree, the aniline derivative tends not to condense with the anthraquinone under the usual reaction conditions. This is most evident when the amine is *p*-nitro aniline or *p*-amino benzoic acid. Nevertheless, it has been possible to prepare a number of derivatives that do contain an electronegative substituent. The amines that were successfully used in this manner are listed in Table III. All of the anthraquinone dyes made from these derivatives of aniline were found to have excellent resistance to gas fading. In no instance was the amino nitrogen sufficiently nucleophilic to be readily subject to attack by nitrogen dioxide. All of these structures were also found to have superior resistance to O fading. Since ozone is a stronger electrophile than the active agent in gas fading, it was found that the charge on the amino nitrogen had to be reduced to a greater degree to obtain satisfactory O fading performance than to obtain satisfactory gas fading performance.

Due to the decreased electron density at the arylamino nitrogen, the shades of the dyes made from the amines listed in Table III are somewhat redder than is usually preferred for a neutral blue. In addition, the affinity for acetate is greatly reduced, which is not surprising because there are many other examples where the introduction of an electronegative group into an anthraquinone molecule reduces the affinity of the molecule for acetate. The affinity of dispersed dyes for any fiber has been related to the size and shape of the dye molecule and of the fiber, as well as to the solubility of the dye in the fiber and in the dyebath [4]. However, the relationships between these properties and the structural electronic characteristics discussed here remain to be established. Even though the amino anthraquinones made from the structures listed in Table III do not have all of the properties needed for a satisfactory dye, they do have a high level of colorfastness and the principles they represent can be applied to the synthesis of other structures that may better satisfy the requirements of a good over-all dye.

## Summary and Conclusions

A correlation has been established between the structure and the colorfastness of disperse anthraquinone dyes on acetate and polyester fibers for a series of arylamino analogs of:

1-hydroxy-4-arylamino anthraquinone
1-hydroxy-4-arylamino-5-hydroxy-8-nitro anthraquinone
1-hydroxy-4-arylamino-8-hydroxy-5-nitro anthraquinone

Colorfastness includes the reaction of these dyes on acetate with both nitrogen dioxide (gas fading) and ozone (O fading) and the photochemical action of light on these dyes on both acetate and polyester fibers.

It has been concluded that the degree of fading exhibited by a given dye structure depends on the nucleophilic characteristics of the arylamino nitrogen. Any structural modification which reduces the electron density on this nitrogen renders it less susceptible to attack by the electrophilic agents responsible for the color changes and vice versa. This conclusion is based on the following general observations.

An —OR substituent (R = H, alkyl, hydroxyalkyl) on the benzene ring para to the arylamino nitrogen produces a dye which fades much more rapidly than does the derivative in which there is an alkyl or a substituted alkyl group in the para position.

An —OR substituent in the meta position on the benzene ring forms a dye with fastness properties that are superior to those of the corresponding para isomer.

Consideration of the active agents in gas fading and in O fading reveals that they are electrophilic by nature and, therefore, would most readily attack a strongly nucleophilic center.

An electron-withdrawing group substituent on the benzene ring para to the arylamino nitrogen produces a dye with a higher resistance to gas fading than the corresponding unsubstituted anilino derivative.

Strong electronegative groups such as $-SO_2NH_2$, $-SO_2N(CH_2CH_2OH)_2$, $-COCH_3$, $-CONH_2$, and $-CF_3$ have been introduced on the arylamino radical in order to reduce the electron density on the arylamino nitrogen far below that of the unsubstituted anilino derivative. Such groups tend to preferentially withdraw electrons from the ortho and para positions on the ring, thus greatly decreasing the nucleophilic character of the arylamino nitrogen. All of the dyes made from these derivatives were found to possess excellent resistance to the action of nitrogen dioxide and of ozone, which is a still more electrophilic reagent. They would also be expected to show a high level of lightfastness on polyester fibers because of the correlation found with other members of this series between gasfastness and lightfastness on polyester. This correlation indicates that the active agent in this color change may also be electrophilic in nature. Application of these concepts to other dye structures has served to explain their behavior towards gas fading.

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# A Comparison of Some Physical Properties of 80x80 Print Cloth Produced from Three Cottons Differing Primarily in Flat Bundle Strength

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## Introduction

In previous reports [4, 5, 8] the authors showed that, while cotton fiber strength has little or no effect on processing efficiency up to spinning, high-strength cotton produces stronger single and 2-ply yarns than low-strength cottons for any given yarn number or twist. A similar study [7] on the effect of mechanical and chemical processing on cotton fiber properties presented sound evidence for the premise that cotton fiber properties influence the behavior of the resultant fabrics.

Because of the need of knowing how fiber properties, particularly flat bundle strength, translate into fabric properties, the cottons used in the above-mentioned studies were processed into a standard fabric. Herein is reported limited data on the effect of cotton fiber strength on the properties of an 80 × 80 print cloth.

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## Materials and Methods

The cottons (Hopi Acala 50, Raingrown A, and Raingrown B) used in the previous studies [4, 5, 8] form the basis for the work covered in this report. Fiber properties of these cottons are summarized in Table I.

While these cottons were primarily selected as representative of the three main strength groups (high, medium, and low), it was a further goal that the other pertinent fiber properties be not too different. The extent to which this was achieved is

**TABLE I. Summary of Fiber Properties**

| Fiber property | Hopi Acala 50 | Raingrown A | Raingrown B |
|---|---|---|---|
| Length | | | |
| Classer, in. | $1\frac{3}{32}$ | $1\frac{3}{32}$ | $1\frac{1}{8}$ |
| Suter-Webb | | | |
| UQ, in. | 1.24 | 1.23 | 1.32 |
| Mean, in. | 1.06 | 1.01 | 1.11 |
| C.V., % | 26 | 31 | 28 |
| Fineness | | | |
| Suter-Webb, μg./in. | 3.90 | 4.10 | 3.90 |
| Micronaire | 4.60 | 4.50 | 3.70 |
| Maturity | | | |
| Sodium hydroxide method, % | 93 | 90 | 75 |
| Strength | | | |
| Pressley Index, lb./mg. | 9.20 | 7.60 | 6.20 |
| Stelometer, g./tex | | | |
| 0 mm. | 44.5 | 39.4 | 34.2 |
| 2.5 mm. | 22.4 | 19.4 | 19.2 |
| Elongation | | | |
| Stelometer, % at 2.5 mm. | 8.0 | 9.0 | 10.7 |

evidenced by the fact that only one independent property, maturity, showed any wide difference among the three cottons. The Micronaire reading is related to Suter-Webb weight fineness and maturity, while elongation is generally found to be inversely related to bundle strength or tenacity.

For all cottons the 30/1 (20 tex) warp yarns were spun with a twist multiplier of 4.40; the 40/1 (15 tex) filling yarns, with a twist multiplier of 3.50. All yarn numbers were controlled as closely as possible in order to make comparison of cotton effects in the fabric as valid as possible. Approximately 75 yd. of a standard 80 × 80 print cloth were woven from each of the three cottons.

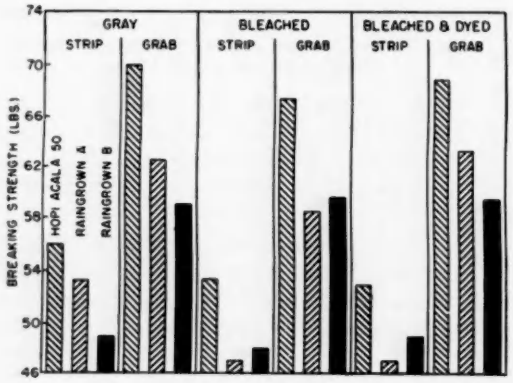


**Fig. 1.** Effect of selected chemical finishing processes on the breaking strength of an 80 × 80 print cloth produced from cottons differing primarily in flat bundle strength (warp direction).

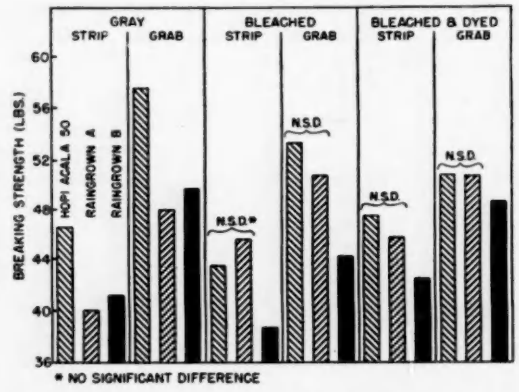


**Fig. 2.** Effect of selected chemical finishing processes on the breaking strength of an 80 × 80 print cloth produced from cottons differing primarily in flat bundle strength (filling direction).

Samples of the gray fabrics were removed; then the remainder was processed at open width on a jig through scouring, bleaching, and dyeing (vat) operations according to normal commercial practices. Samples were taken of the bleached portion before dyeing.

All tests and test conditions were in accordance with ASTM specifications [1]. In particular, the fabrics were tested for strength by the strip and grab methods [1a] on a pendulum type tester and for resistance to tearing by the Elmendorf method [1b]. Strip tests were based on 80 threads per inch for all samples. Abrasion tests were made by the flexing and abrasion method [1c].

## Analysis of Data

The data and consequently the conclusions are necessarily limited, since they are based on cottons of only three strength levels evaluated in a standard 80 × 80 print cloth. Breaking strength values are shown in Figures 1 and 2.

In Figure 1 it is shown that the strongest-fibered cotton produced the strongest fabric, regardless of the state of the fabric or method of test (strip or grab) for samples taken in the warp direction. However, for samples taken in the filling direction (Figure 2), only in the gray state does the strongest-fibered cotton exhibit its superiority. This could be due to the fact that at the low spinning twist used (3.50 T.M.), the amount of interfiber bonding required for the potential of fiber strength to be realized in yarn strength has not been attained. Although the strongest-fibered cotton made the strongest fabric (fillingwise) in the gray state, the low amount of twist in the filling yarns probably prevented the resistance to a leveling-out effect of the chemical finishing processes. Statistical tests for significance of difference of fabric strength in the warp and filling directions showed, except as noted in Figure 2, that the fabric made from the strongest-fibered cotton was significantly stronger (at 95% level or higher) than the fabric made from the cotton next below it in fiber strength.

That the cotton designated as Raingrown A did not always provide fabrics having intermediate strength values may be explained by the fact that yarn strength—and for the purpose of this report, presumably fabric strength—has been shown [2, 3] to correlate more closely with cotton fiber bundle tenacity values obtained at a finite gauge spacing

than when zero gauge spacing is used. In such a case it may well be that the ranking of these cottons by Stelometer [2] tests at 2.5 mm. permits the best estimate of fabric strength ranking. Then, with two cottons having strength values so nearly alike as do Raingrown A and B, it is possible that the strength values of fabrics made from them could vary, due to changes in fabric geometry induced by chemical finishing processes.

This failure of these fabrics, based on tests made on fillingwise samples, to maintain, through chemical processing, the strength ranking of the fibers does not exactly agree with other findings in this field [7]. Through scouring, bleaching and mercerizing, and resin finishing it was reported [7] that the relative strengths of fabrics made from high, intermediate, and low strength cottons were in the same order as for the fiber breaking stress. However, since the data were reported in terms of overall fabric strength, it is impossible to determine whether the conclusions drawn were significantly different from those of this investigation.

Elongation at break values are contained in Figure 3. Except for samples taken in the filling direction from the bleached and dyed fabric, practically no differences or trends are seen among the three fabrics either warp or fillingwise. This, too, does not agree with previous findings [7], where fabric breaking elongation, through several chemical finishing processes, maintained the same ranking as for the fiber breaking elongation.

It is interesting to note that even though Raingrown B cotton had shown higher elongation values for fibers and single and 2-ply yarns [4, 5], this difference did not carry over into the fabrics. However, it was observed during the finishing operation on a standard jig that the fillingwise shrinkage of the fabric produced from the Raingrown B cotton was over twice that observed for the other two fabrics. However, the magnitude of this difference wasn't maintained after drying on the tenter frame. An index of the progressive shrinkage across the width of the fabric can be seen (Figure 3) from the resultant progressive increase in fabric elongation at break of samples taken from the filling from the gray state through the bleached and bleached and dyed

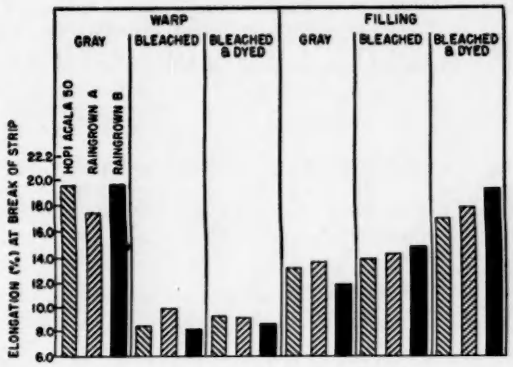


**Fig. 3.** Effect of selected chemical finishing processes on the elongation at break of raveled strips of an 80 × 80 print cloth produced from cottons differing primarily in flat bundle strength (warp and filling directions).

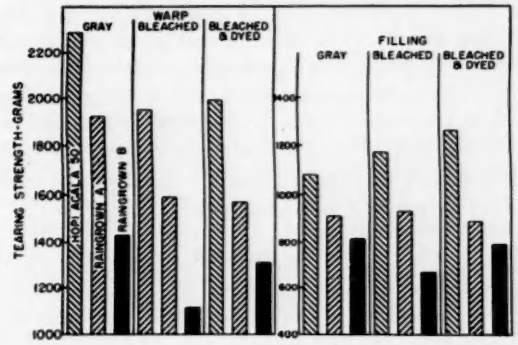


**Fig. 4.** Effect of selected chemical finishing processes on the resistance to the Elmendorf Tearing Test of an 80 × 80 print cloth produced from cottons differing primarily in flat bundle strength (warp and filling directions).

states. Since differences in elongation of the fibers were not reflected in differences in elongation of the fabrics in the gray state, this progressive increase in fabric elongation at break fillingwise is probably due, in part, to the continuous warpwise tension to which the fabric was subjected during finishing on the jig with the effect of inducing progressive reduction in width.

Results from the Elmendorf Tear Resistance Test (Figure 4) show that the fabrics made from the three cottons assume a ranking which is consistent with tenacity values obtained at zero gauge (both Pressley and Stelometer) in both warp and filling directions and regardless of the state of the cloth. That this test ranks these fabric samples consistently in the order of fiber tenacity values may in a limited way provide additional support for the growing trend

[2] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

**TABLE II. Effect of Selected Chemical Finishing Processes on the Resistance to Abrasion of an 80 × 80 Print Cloth Produced from Cottons Differing Primarily in Flat Bundle Strength (Warp and Filling Directions)**

| | Abrasion cycles* | | | | | |
|---|---|---|---|---|---|---|
| | Warp | | | Filling | | |
| Variety | Gray | Bleached | Bleached and dyed | Gray | Bleached | Bleached and dyed |
| Hopi Acala 50 | 1513 | 718 | 718 | 1470 | 602 | 583 |
| Raingrown A | 1272 | 511 | 204 | 1122 | 266 | 167 |
| Raingrown B | 1484 | 947 | 878 | 930 | 738 | 530 |

* 3 lb. on bar; 1½ lb. on plate.

toward the selective use of this test for evaluating the strength characteristics of woven fabrics.

Table II shows abrasion resistance values for the 80 × 80 print cloths produced from cottons differing in flat bundle strength and elongation evaluated in the gray, bleached, and bleached and dyed states. There appears to be no relationship between cotton fiber strength or fabric strength and fabric abrasion resistance after any of these stages of processing. Of significance is the large decrease in abrasion resistance of the Raingrown A fabric from the gray state to either the bleached or the bleached and dyed state, both warp and fillingwise.

## Conclusions

Based on evaluations of the 80 × 80 print cloth fabrics produced in this investigation, the following conclusions may be drawn.

1. The strongest-fibered cotton produced the strongest fabrics in the warp direction in the gray, bleached, and bleached and dyed states; however, in the filling direction this relationship did not hold for the bleached and bleached and dyed states.

2. Elongation at break of fabrics (raveled strips) was apparently influenced more by mechanical treatment during chemical processing than by fiber properties.

3. Tearing resistance of the fabrics appeared to be correlated with cotton fiber strength at zero gauge.

4. There appeared to be no relationship between cotton fiber strength and fabric abrasion resistance except in the filling direction in the gray state.

## Acknowledgment

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# Preparation and Rates of Hydrolysis of Perfluoro-Esters of Cellulose

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**Abstract**

Partial esters of cellulose varying in degree of substitution from 0.02 to 0.58 were prepared by reacting cellulose immersed in dimethylformamide with either perfluorobutyryl chloride or perfluorooctanoyl chloride in the presence of a tertiary aromatic amine. The use of essentially homogeneous solutions of acid chlorides resulted in products which retained properties of the original cotton and showed in addition oil and water repellency which was durable to dry cleanings and aqueous launderings in the presence of neutral detergents. Rates of uncatalyzed hydrolysis of the perfluorooctanoyl cellulose esters were determined at 25°, 35°, and 45° C., and the rate of the alkaline catalyzed hydrolysis was estimated at 25° C. The energy and entropy of activation for the uncatalyzed hydrolysis were determined.

## Introduction

The application of fluorochemicals to textiles has been under study for several years at the Southern Regional Research Laboratory [9, 12]. Although excellent oil and water repellent finishes were obtained in many instances, these surface treatments were not durable to conventional launderings. The oil repellency was not affected by exposure to organic solvents at 25° C., but was removed by extractions in boiling organic solvents. Aqueous launderings, even with neutral detergents, reduced the effectiveness of even the best finishes. The present investigation is concerned with the esterification of cotton cellulose with perfluoro-acid chlorides to produces partial esters of cellulose having more durable finishes and the determination of the rates of hydrolysis of these partial esters.

The majority of literature references on the hydrolysis of esters is concerned with the alkaline or acid catalyzed reactions and allows the qualitative prediction of the effect of structure upon hydrolysis rates [2, 5]. In esters of perfluorinated carboxylic acids, the electron attracting perfluoro moiety has a great effect upon the carbonyl carbon. It is at this carbonyl carbon that the anion attacks in base catalyzed hydrolysis before the attack of a water molecule at the alkyl oxygen where the effect of the perfluoro moiety is damped. In acid hydrolysis, the proton attacks at the alkyl oxygen remote from the perfluoro substituent, and the water molecule attacks at the carbonyl oxygen.

Usually the attack by water molecules is less important than the acid or base catalyzed steps. As the electron attracting properties of the alkyl group adjacent to the carbonyl of the ester increases, the attack by water molecules becomes the rate-determining step. If the effects of substituents were the only rate-determining factors, perfluoro esters should hydrolyze rapidly even in the absence of catalysts. However, perfluoro compounds exhibit unusual solubility properties. If the perfluoro ester is insoluble in water, it is not easily hydrolyzed. For example, Hauptschein [4], in a study of the stability of the esters derived from perfluoro mono- and dicarboxylic acids and perfluoroalcohols, found that certain mono- and diesters which were insoluble in water were only slowly hydrolyzed even in 10% sodium carbonate solutions in spite of the fact that they contained a perfluoro moiety alpha to the carbonyl group. However, these perfluoro esters are rapidly saponified in 10% potassium hydroxide solution. Even for insoluble esters, it is necessary that the perfluoro group be shielded from the carbonyl group by at least one $CH_2$ group if the ester is to show no signs of hydrolysis in 5% aqueous potassium hydroxide [3].

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Perfluorohydrocarbons have limited miscibility with hydrocarbons and halogenated hydrocarbons. Simons [13] has attempted to explain the repulsion in terms of an interpenetration model. Those perfluoroacids which show low water solubility have been shown by the work of Cottington [1] to form highly oriented monolayers on metal surfaces.

Moffat and Hunt [7] in their studies of the effects of substituents upon the rates of hydrolysis of fluorinated esters of the types $CF_3COOR$ and $R_FCOOC_2H_5$, where R and $R_F$ are the alkyl and perfluorinated alkyl groups, respectively, derived two equations which relate the change in specific reaction rate constants to the change in molecular weight of the R groups. In brief, the rate of hydrolysis of both types of esters decrease with increase in weight of the R group. These studies indicate that the large molecular weight of cellulose should favor low rates of hydrolysis of the perfluoroesters of cellulose, and a long chain length of the perfluoro carbon portion of the acid used should produce oil and water repellency which would resist hydrolytic and solvolytic degradation of the perfluoroesters of cellulose. The rates of hydrolysis of perfluorooctanoic esters of cellulose determined in this investigation are in accord with these previous findings.

## Materials

### *Fabric Description*

The cotton materials used were a bleached 80 × 80 print cloth weighing 3.12 oz./sq. yd. and a 48 × 48 sheeting weighing 4.18 oz./sq. yd. Both fabrics were processed in commercial peroxide bleaching equipment. A 7/2 mercerized yarn was used.[3]

### *Chemicals*

The pyridine, dimethylaniline, and benzene were reagent grade chemicals obtained from the J. T. Baker Chemical Co., and the dimethylformamide was Eastman's reagent grade.[3] The neutral detergent used was Procter and Gamble's Joy.[3]

The oils used for testing were U.S.P. white mineral oil, S.A.E. No. 10 lubricating oil, paraffin oil, a refined cottonseed oil, and a refined olive oil.

The perfluoroalkanoic acids were reagent grade chemicals obtained from Columbia Organic Chemicals Co.,[3] and were used as such for the preparation of the perfluoroalkanoyl chloride. The perfluoroalkanoic acids were refluxed with thionyl chloride in the presence of a minute quantity of pyridine, which was used as a catalyst. The perfluorobutyryl chloride fraction boiling at 38–39° C. and the perfluorooctanoyl chloride fraction boiling at 129–130° C. (744 mm.) were used [6] in the esterification processes.

[3] Trade names have been used only to identify equipment or materials actually used in conducting this work. Their use does not imply endorsement or recommendation by the U. S. Department of Agriculture over other similar products not mentioned.

## Experimental

### *Preparation of Partial Esters of Cellulose*

The method of esterification is important in producing uniformity of treatment. Obviously, the less heterogeneous the acid chloride solution, the greater the likelihood of uniform esterification and the greater will be the chances of covering the surface of the cotton with oriented perfluorocarbon chains which will prevent the approach of hydrolytic solvent molecules to the ester bonds. The choice of solvent for the esterification process is difficult because of the very limited solubility of the perfluoroalkanoyl esterifying agents.

Preliminary esterification reactions with pyridine and the perfluoro acid chlorides showed initial precipitation of salts which dissolve only in a very large excess of pyridine. Therefore, the use of a nonhydroxylic solvent of high dielectric constant was indicated in order to increase the solubility of the reacting ion. Dimethylformamide proved to be such a medium. The concentration of pyridinium complex of the acid chloride in dimethylformamide could be built up to such a value as to permit rapid reaction at room temperature. In some experiments, an excess of pyridine was employed as an acid scavenger. The pyridine along with the dimethylformamide aided in swelling and dehydrating the cotton, thus facilitating a more rapid and uniform reaction.

On occasion, when N,N-dimethylaniline was used in the place of pyridine, the amine was dissolved in several parts of dimethylformamide prior to adding it to the reaction mixture.

It is usually unnecessary and uneconomical to employ large amounts of the perfluoroalkanoyl halide, as the desired oleophobic and hydrophobic properties can be achieved at low degrees of substitution of the cellulosic material. In general, the cotton sample is immersed in dimethylformamide before the esterifying agent is dissolved in the dimethylformamide. Following this, just enough tertiary aromatic amine

is added to neutralize any acid formed during the esterification reaction. The order of addition of the reactants is of prime importance and must be followed. It is unsatisfactory, for example, to dissolve the esterifying agent in a dimethylformamide and pyridine solution and then treat the cotton with the resultant solution. If the latter procedure is used, there is considerable loss in the tensile strength of the fabric and the oil repellency is poor.

A typical experimental procedure for the preparation of an excellent oleophobic and hydrophobic finish is as follows. A 1.2-g. sample of 80 × 80 scoured and bleached cotton fabric was thoroughly wetted with 5 ml. of dimethylformamide at 25° C. in a 100-ml. round bottom flask. Then 2 ml. of perfluorooctanoyl chloride (B.P. 130° C. at 744 mm.) was added while the flask was being shaken. This was followed by the addition of 1 ml. of pyridine. After a reaction time of 4 min., the fabric was washed for 2–3 min. in tap water (25–30° C.), then methanol, then tap water again. The fabric was dried in an oven maintained at 90° C. The resultant fabric had a weight gain of 27% (DS of 0.10) and physical properties like those of the original fabric; that is, its tear strength, color, appearance, hand, and fibrous structure were not altered much by the treatment. In addition, it possessed excellent oil and good water repellent properties which were durable to 1-hr. soxhlet extractions with carbon tetrachloride or ethanol as well as to two water boils of 20 min. duration in the presence of a neutral detergent.

### *Tests for Oil and Water Repellency*

For evaluation of oleophobic and hydrophobic properties of the treated fabrics, the method employed earlier [9] of placing the fabric on a plate glass mounted above a mirror and placing the drops of liquids on these mounted fabrics was used. If the drops of oil stood for a week or longer without penetration of the fabric, the sample was said to have excellent oil repellency. Hydrophobic properties were evaluated similarly with drops of water placed on the fabric samples. The fabric was said to have good water repellency if the drops stand for at least 8 hr. without penetration of the fabric.

### *Infrared Analyses*

The potassium bromide disc technique was used for the measurement of the infrared spectra of the cotton fabric and perfluorooctanoyl esterified fabrics according to the method of O'Connor et al. [8].

### *Rates of Hydrolysis*

The top of a 100-ml. capacity weighing bottle (40 × 80 mm.) was fitted to accommodate a dipping type conductivity cell, the inlet, and the outlet for nitrogen gas. The constant for the conductivity cell used was 0.09596 $cm.^{-1}$. Conductivity water (50 ml.) was placed in the conductivity cell in a constant temperature bath and allowed to equilibrate. Throughout all measurements, dry nitrogen was bubbled through conductivity water before entering the conductivity cell in order to saturate the nitrogen with water vapor to maintain a constant volume of water in the cell. A commercial type of conductivity bridge (Industrial Instrument, Inc., Model RC-1B) [3] was used. After the conductance of the water had been measured, a sample of the perfluorooctanoyl ester of cellulose was placed in the cell. A period of 5 min. was allowed for the cell and contents to reach the temperature of the bath before the first reading was taken. The specific conductance at infinite time was determined after allowing the cell and contents to stand in an inert atmosphere until the conductance reached a constant value. The rates of neutral hydrolysis, that is, hydrolysis not catalyzed by an external acid or base, of the cellulose esters of perfluorooctanoic acid were determined at 25°, 35°, and 45° C.

The rate of hydrolysis of the perfluorooctanoyl cellulose ester was also estimated in a more basic medium at 25° C. in order to compare this rate with the rate of the self-catalyzed reaction. In the former, the milliequivalents of perfluorooctanoic acid liberated by the hydrolysis of the ester during various timed intervals were titrated with a standard NaOH solution. The samples of the perfluorooctanoyl cellulose were weighed before and after the hydrolysis, and the loss in weight was compared with the loss in weight as determined by the milliequivalents of standard base used in the titrations. The pH of the solution was kept at approximately 7.5 during the short period required for approximately two-thirds of the ester to hydrolyze.

## Results and Discussion

### *Products of Preferred Method of Esterification*

Under the specific conditions of esterification, oil and water repellent cotton fabrics can be produced

**TABLE I. Partial Esterification of Cotton with Perfluoroalkanoyl Chloride* in the Presence of Dimethylformamide and Pyridine at 25° C.**

| Sample number | Description | Reaction time, min. | Weight gain, % | D.S. (calculated) | Mole ratio $C_6H_{10}O_5$:Acid chloride:Pyridine:DMFA |
|---|---|---|---|---|---|
| 1 | 80 × 80 | 60 | 47 | 0.37 | 1:0.8:1.3:6 |
| 2 | 80 × 80 | 75 | 114 | 0.45 | 1:0.8:1.3:6 |
| 3 | 80 × 80 | 75 | 138 | 0.55 | 1:0.8:1.3:6 |
| 4 | 80 × 80 | 75 | 145 | 0.58 | 1:0.8:1.3:6 |
| 5 | 48 × 48 | 45 | 4 | 0.02 | 1:0.8:2.6:12 |
| 6 | 48 × 48 | 210 | 7 | 0.03 | 1:0.8:2.6:12 |
| 7 | 48 × 48 | 900 | 27 | 0.12 | 1:0.8:2.6:6 |
| 8 | 80 × 80 | 3 | 4 | 0.02 | 1:1:2:9 |
| 9 | 80 × 80 | 4 | 27 | 0.12 | 1:1:2:9 |
| 10 | 48 × 48 | 45 | 8 | 0.04 | 1:1.4:2.4:14 |
| 11 | 48 × 48 | 50 | 9 | 0.04 | 1:1:4:18 |
| 12 | 48 × 48 | 60 | 6 | 0.03 | 1:1:4:18 |
| 13 | 80 × 80 | 780 | 26 | 0.12 | 1:1:1:20† |
| 14 | 2-ply yarn | 60 | 30 | 0.13 | 1:2.5:9:3.5 |

* All data for perfluorooctanoyl chloride except sample 12, which is for perfluorobutyryl chloride.
† N′,N′-dimethylaniline used in place of pyridine.

in reaction times as low as 3 min. at 25° C. The finish which is durable to drycleaning and aqueous launderings in the presence of neutral detergents is achieved at extremely low degrees of substitution. However, higher degrees of substitution without significant alteration of strength, color, or hand can be achieved by this method. Esters listed in Table I are representative of the method and all showed excellent oil and good water repellency. Because of the scarcity of the perfluorochemicals, not all experiments were performed with fabric samples large enough for complete textile testing. Representative samples of the partial esters retained 70–80% of their original breaking strengths as tested with the Instron Tensile Tester. Reaction times are not as important as the molar ratios of the reactants, and low degrees of substitution can be obtained even after 15 hr. of reaction time without loss of the original fabric properties. Oleophobic and hydrophobic finishes were obtained with both the perfluorobutyryl and perfluorooctanoyl esters, but the latter gave a finish which was more durable to aqueous boils in the presence of neutral detergents. Both esters were hydrolyzed in aqueous boils in the presence of alkaline detergents.

Samples of higher degrees of substitution were used for the infrared analyses. A band at 5.63$\mu$, characteristic of the C = O group in perfluoroester linkages, was observed with the perfluorooctanoyl cellulose samples 3, 12, and 13 of Table I. The normal C = O stretching vibration of esters results in an absorption band at 5.75$\mu$. In nonfluorinated unconjugated esters, electronegative alpha substituents, by virtue of the inductive effect, shift the absorption wave length only as low as 5.70$\mu$ [11]. Rapapport et al. [10] have shown the effects of neighboring fluorine atoms on the ester carbonyl frequency. These investigators report a shift to 5.66$\mu$ in compounds of the type $RC(=O)-OCH_2-R_F$ where the fluorines are removed by a $(-\underset{H}{\overset{H}{C}}-O)$ group from the carbonyl group, and a shift to 5.60$\mu$ when the perfluoro moiety is alpha to the carbonyl group, as it is in the perfluorooctanoyl cellulose ester. Strong absorption bands were also observed at 8.33$\mu$ and 8.73$\mu$, which are characteristic of C—F bonds and not observed in unmodified cottons. Changes in intensities of these characteristic bands with degree of esterification for the partial esters of perfluorooctanoyl cellulose are given in Table II. These values have been corrected for differences in sample weights.

Portions of sample 8 (Table I) were analyzed for the percentage of fluorine and found to contain 3.13% fluorine. This sample retained 80% of its original breaking strength as tested with the Instron Tensile Tester.

Microscopial observations indicated that the partial esterification was a surface treatment; the reaction did not take place throughout the entire fiber structure. Electron micrographs of unmodified cotton fibers and fibers esterified with perfluorooctanoyl chloride to a weight gain of 30% are shown in Figure 1. It is apparent that the surface of the partially esterified fiber is smoother than is the surface of the untreated cotton, and only a few areas appear to be disturbed or swollen.

An x-ray diffraction pattern of a fiber bundle of this perfluorooctanoyl cellulose ester showed it to have the same crystalline pattern as the original cellulose.

Microscopial examination of fabrics esterified to 6% and 30% weight gains were made after the samples were dyed with alkaline ruthenium red and with methylene blue. Significantly greater uptake of dye by the esterified samples than by the control cotton was observed. Even though these basic dyes showed an uneven distribution of stained areas, probably due to hydrolysis of the ester linkages, it was apparent that the stained material was on the surface of the fibers only.

*Use of Other Methods of Esterification*

A 2.23-g. sample of 80 × 80 scoured and bleached cotton fabric was treated with 9 g. of perfluorobutyryl chloride (B.P. 38–39° C. at 744 mm.) in 45 ml. of pyridine by immersing the cotton in the treating solution for 1 hr. at 25° C. The treated fabric was washed in pyridine, then acetone, and then dried 16 hr. at 25° C. The resultant fabric had a 167% weight gain (DS 1.3) and a very poor tear strength; was rough in hand, stiff, and slightly yellow; and possessed some oil and water repellency. However, after a 20-min. aqueous boil with a neutral detergent, the fabric lost 17% by weight, and the oil and water repellent properties of the fabric were greatly reduced. Oil droplets spread and wet the fabric in less than 3 min. After a second aqueous boil in the presence of a neutral detergent, the fabric completely lost its oil repellency, but was still water repellent. The oil repellent properties were decreased considerably when the fabric was subjected to 1-hr. extractions in either carbon tetrachloride or ethanol. In similar experiments where the anhydroglucose : perfluoroalkanoyl chloride : pyridine ra-

**TABLE II. Increase in Intensity of Infrared Spectral Bands Characteristic of Perfluoro Substituents with Degree of Esterification for Perfluorooctanoyl Cellulose**

| | Percent transmittance | | |
|---|---|---|---|
| | Bands (μ) | | |
| DS | 5.63 | 8.33 | 8.73 |
| 0.03 | 88.0 | 35.4 | — |
| 0.16 | 57.5 | 26.0 | 27.0 |
| 0.45 | 32.2 | 11.0 | 11.6 |
| 0.55 | 29.7 | 8.2 | 9.0 |

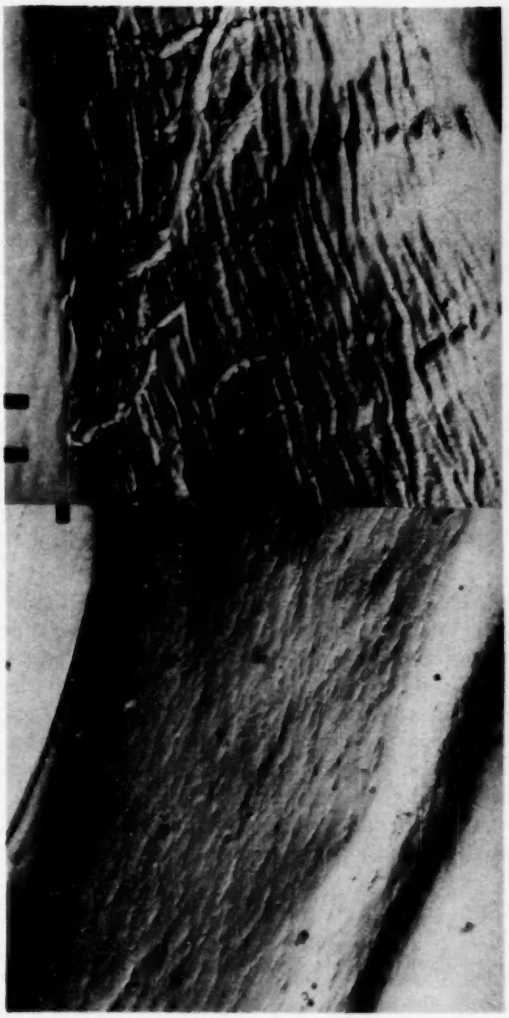

**Fig. 1.** Electron micrographs of surface replicas obtained by the polystyrene–carbon method; platinum (80%) palladium (20%) shadowing. Top: control, 8000 ×. Bottom: perfluorooctanoyl cellulose (DS 0.13).

tios were 1:3:57, the solutions of acid chlorides were not homogeneous as in the preferred method of using dimethylformamide as the solvent. If the reaction was allowed to take place over an extended period, for example, 15 hr., the fabric was completely disintegrated when pyridine alone was used as the solvent, whereas the fabric properties remained essentially unaltered after 15 hr. of reaction according to the preferred method of esterification in dimethylformamide.

The use of solvents other than dimethylformamide at various temperatures and mole ratios of reactants was investigated. In most instances, heterogeneous reaction mixtures resulted in spotty finishes on fabrics of greatly reduced breaking strengths. When benzene was used as the solvent in the mole ratios similar to those given in Example 13 of Table I, a homogeneous solution of acid chlorides was obtained at 70° C., and weight gains of 1–6% resulted in good oil and water repellent finishes. However, all fabrics esterified with benzene as the solvent suffered considerable losses in breaking strengths.

*Reaction Kinetics of Perfluorooctanoyl Cellulose*

The hydrolysis reactions were found to follow a pseudo first order relationship, and the specific reaction rate constant $k$ was calculated at each temperature according to the following equation:

$$k = \frac{1}{t_2 - t_1} \ln (C_\infty - C_1)/(C_\infty - C_2)$$

where $C_1$, $C_2$, and $C_\infty$ are the specific conductances at times $t_1$, $t_2$, and infinity respectively. Several determinations were made at each temperature, and log $(C_\infty - C_1)$ was found to vary linearly with time. The values of $k$ recorded in Table III were calculated from the slopes of the lines as obtained by the Method of Least Squares applied to all experimental points at each temperature.

The activation energy, $\Delta E^*$, was derived in the usual way from the following equation:

$$k = (PZ) \exp (-\Delta E^*/RT)$$

where $k$ is the specific reaction rate constant, $(PZ)$ is the frequency factor, $R$ is the molar gas constant, and $T$ the absolute temperature. The values of $k$, $\Delta E^*$, and $\Delta S^*$ are given in Table III for the self-catalyzed hydrolysis rates. A plot of log $k$ against $1/T$ gave a straight line, the equation of which was calculated by the Method of Least Squares. The slope of the line was found to be $-803.6$, and $\Delta E^*$ was calculated to be 3.68 kcal./mole. This low energy of activation indicates that, once the water reaches the ester linkage, the ester bond is easily broken. Apparently the water molecules do not reach the ester linkages easily. Probably stability of the perfluoro ester of cellulose is due to the orientation of the perfluoro chains which hinder the approach of water molecules.

Since the concentration of the liberated acid was small in all cases, there was no apparent curvature in the plot of specific conductance vs. acid concentration; therefore, no corrections were made. The reaction studies were followed to 67% completion of hydrolysis without changes in the rate constants.

The entropy of activation was calculated from the equation

$$\Delta S^* = R\left[\ln k_1 - \ln\left(\frac{KT}{h}\right) + \frac{\Delta E^*}{RT} - 1\right]$$

where $k_1$ is the hydrolysis constant in sec.$^{-1}$, $E$ is the energy of activation as obtained from the plot of ln $k$ vs. $1/T$, and $R$, $k$, and $h$ are the molar gas,

**TABLE III. Specific Reaction Rated Constant, Activation Energy, and Entropy of Activation of the Non-Catalyzed Hydrolysis of Perfluorooctanoyl Cellulose Dedermined Conductimetrically**

| Temperature, ° C. | $k$, × 10$^5$ sec.$^{-1}$ | $\Delta E^*$,[a] kcal./mole | $\Delta S^*$,[b] cal./mole deg. |
|---|---|---|---|
| 25 | 1.52 | | |
| 35 | 1.85 | 3.7 | −69.9 |
| 45 | 2.28 | | |

[a] Calculated from slope of straight line (ln $k_1$ vs. $1/T$) as calculated from Method of Least Squares.

[b] Entropy of activation calculated from $\Delta S^* = R[\ln k_1 - \ln (kT/h) + (\Delta E^*/RT) - 1]$.

**TABLE IV. Hydrolysis of Perfluorooctanoyl Cellulose at pH 7.5 Determined Titrimetrically**

| | Samples | |
|---|---|---|
| | A | B |
| Degree of substitution | 0.21 | 0.36 |
| Total acid esterified on sample, mg. | 342.7 | 428.0 |
| Acid titrated, mg. | 230.2 | 207.0 |
| Weight loss of sample, mg. | — | 230.0 |
| Ester hydrolyzed, % | 67.0 | 48.0 |
| Specific reaction rate constant, sec.$^{-1}$ | $5 \times 10^{-2}$ | $3 \times 10^{-2}$ |

Boltzman, and Planck constants respectively. The large negative value of $\Delta S^*$ is similar to that calculated from the data given in Moffat's paper [7] for the uncatalyzed hydrolysis of the esters of perfluoroacetic acid.

As usual, the rate of hydrolysis in the alkaline medium was much faster than in the neutral or acid media. At 25° C., the specific reaction rate constant was approximately a thousandfold greater than in the uncatalyzed hydrolysis reaction. Again, the reaction followed a pseudo first order rate; the reaction rate constant was calculated to be $3 \times 10^{-2}$ sec.$^{-1}$ and $5 \times 10^{-2}$ sec.$^{-1}$ at 25° C., as shown in Table IV.

The low value of the energy of activation is one explanation for the loss in oil repellency when a hot (160° F.) water wash is used to remove excess reactants and solvents after the esterification process. Probably, at the higher temperature, the water molecules are soluble enough in the excess reactants to reach the ester bonds. Once the excess reagents are removed with cold water and alcohol, further washes in hot water can be made without loss of the oil repellency.

## Summary

Partial esters ranging from 0.02 to 0.58 in the degree of substitution were prepared by reacting cellulose with either perfluorooctanoyl chloride or perfluorobutyryl chloride in dimethylformamide as a solvent and in the presence of a tertiary aromatic amine as the basic catalyst. The resultant esters had excellent oil and good water repellent finishes which were durable to drycleaning and aqueous launderings in the presence of a neutral detergent. The noncatalyzed hydrolysis rates for the perfluorooctanoyl cellulose esters were followed conductimetrically at 25°, 35°, and 45° C. The alkaline-catalyzed hydrolysis rate at 25° C. was followed titrimetrically. All hydrolysis rates followed pseudo first order reaction kinetics. The energy of activation was 3.7 kcal./mole for the uncatalyzed hydrolysis, and the rate of hydrolysis was a thousandfold faster in the alkaline medium than in the uncatalyzed medium at 25° C.

## Acknowledgments

The authors wish to express their appreciation to Miss Elizabeth R. McCall for the infrared spectrophotometric curves, Mr. Paul J. Murphy for the fluorine analyses, Miss Anna T. Moore and Mr. Verne W. Tripp for the photomicrographs, Mr. Charles J. Conner for some of the preparations of perfluorooctanoyl chloride, and Mr. Joseph J. Creely for the x-ray diffraction patterns.

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*Manuscript received November 9, 1959.*

# Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

## Correlation of Instron and Elmendorf Tearing Strength Results

Harris Research Laboratories, Inc.
6220 Kansas Avenue, N. E.
Washington 11, D. C.
January 14, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

Quartermaster investigators have discussed the importance of tearing strength testing for the prediction of the service life of fabrics and have indicated a preference for the Elmendorf method over the single rip, tongue tear method on a Scott pendulum tester [1, 4, 7]. In recent years, the Instron tester has been used frequently for the tongue tear test; the graph thus obtained allows a more detailed study of the tear mechanism, and the nearly inertialess system reduces certain errors inherent in the pendulum tester. Krook and Fox [2], Painter et al. [3], Texeira et al. [8], and Steele [5] have analyzed the mechanism of fabric tear. The Elmendorf scale reading was shown to be essentially an expression of work [2], while the Instron charts are usually evaluated in terms of locations of peaks and/or valleys, which represent tearing force. The Elmendorf test was shown to proceed at 100–150 times the rate of the Instron test [5].

Steele [5, 6] found the Instron test to be more sensitive to deformability of the fabrics, such as caused by softener application; in studying a series of softeners applied to a fabric, he obtained differences in results of 80% with the Instron and 40% with the Elmendorf tester. Hynek and Buri [1] found good correlation between Instron and Elmendorf tests on cotton uniform fabrics, with the Elmendorf results higher than the Instron values. Smith and Brandt [4] found good agreement between the tests for a 80/20 cotton/nylon fabric, but in the case of an all-cotton poplin, the Instron gave higher values.

The present work was undertaken to investigate the correlation between the Instron and Elmendorf method for a group of fabrics covering a rather broad range of weights, weaves, finishes, component fiber types, and testing conditions. While the Instron method is an excellent analytical tool, the Elmendorf method is practical and expedient. Hence, it was of interest to determine whether the Elmendorf device could be used in place of the Instron without undue loss of information for the purposes of routine testing.

Included in the present comparison were cotton fabrics ranging from 3 to 10 oz./sq.yd. in plain, sateen, and twill weaves. These were finished in a variety of ways: grey, plain finish, Sanforized, mercerized, and/or bleached; most were available also in the resin treated state. One 100% spun viscose and one cotton/viscose blend was included, as were fabrics with cotton in the warp and cotton/nylon blends in the filling.

Elmendorf tearing strength measurements were made according to ASTM D1424-56T. The length of tear was 1¾ in. Single rip, tongue tear measurements (ASTM D-39-49) were made on an Instron tester at a rate of 12 in./min., and the actual length of tear was again 1¾ in. From the graphic record, a visual estimate of the average load (average of peaks and valleys) was made and converted to grams.

In Figure 1, the Elmendorf tearing strength values were plotted against the corresponding Instron

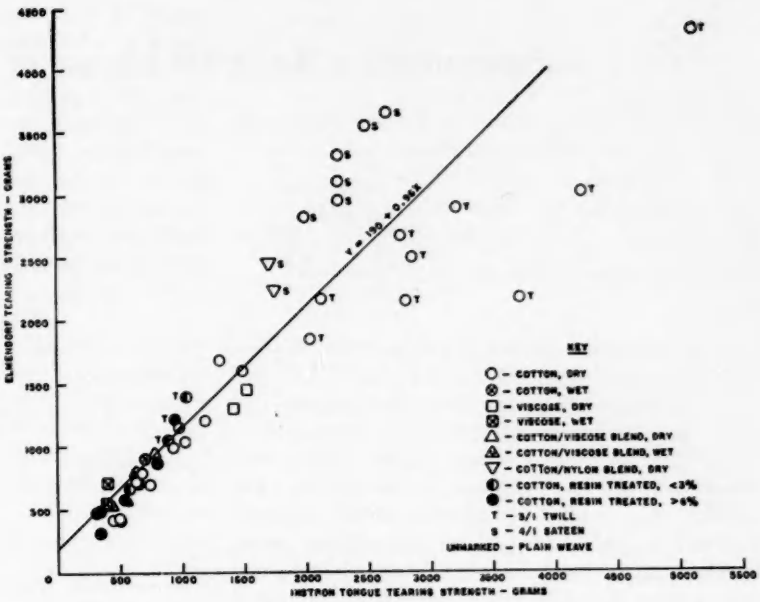
ELMENDORF TEARING STRENGTH – GRAMS
INSTRON TONGUE TEARING STRENGTH – GRAMS
KEY
○ – COTTON, DRY
⊗ – COTTON, WET
□ – VISCOSE, DRY
⊠ – VISCOSE, WET
△ – COTTON/VISCOSE BLEND, DRY
▲ – COTTON/VISCOSE BLEND, WET
▽ – COTTON/NYLON BLEND, DRY
◐ – COTTON, RESIN TREATED, <3%
● – COTTON, RESIN TREATED, >6%
T – 3/1 TWILL
S – 4/1 SATEEN
UNMARKED – PLAIN WEAVE

**Fig. 1.** Relationship between Instron and Elmendorf tearing strength results.

values, warp and filling separately. The data could be fitted [1] by a line:

Elmendorf tearing strength, g. = 190 + 0.96 Instron tongue tearing strength.

The intercept is not statistically significant. The points up to about 2000 g. tearing strength, which represent mostly plain weave fabrics (plain and resin finished cotton, rayon, cotton/rayon blends dry and wet), and resin treated cotton twills, were close to this line. Above 2000 g. the deviations from the line increased considerably: all points representing 3/1 twills were below and all five-shaft sateens above the general line. This indicates that better fit of the points could be obtained by separate lines for the fabrics of each weave; however, even the correlation for all fabrics, regardless of weave, was highly significant, the correlation coefficient being 0.89.

As previously indicated, the Instron tongue tear values are visually estimated average load values. Many investigators feel justified in using only the average maximum load (average of peaks from chart); others advocate the use of the average minimum load (average of valleys from chart). Our experience has shown that the choice of maximum or minimum load shifts the line along the Instron axis but affects the slope only slightly.

In summary it may be said that, in lower tearing strength regions, the Elmendorf results correlated well with the Instron tongue tear results; at higher tearing strength levels, a distinct effect of weave appeared, with an opener weave rating relatively high and a somewhat tighter weave relatively low on the Elmendorf scale.

[1] Due to paucity of data in the higher regions, only tearing strength values below 4000 g. were considered.

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J. F. KRASNY
D. C. BORTON

# Correspondence Regarding Segal et al. Paper

The State Institute for Technical Research
Chemico-Technical Laboratory
Helsinki, Finland
December 14, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In a recently published research report in this journal, Segal, Creely, Martin, and Conrad [4] presented an empirical method for estimating the degree of crystallinity of native cellulose, using a Norelco 90° x-ray diffractometer. These authors expressed the percent crystalline material in the total cellulose by an x-ray "Crystallinity Index," abbreviated CrI. Their "Crystallinity Index" was based upon the intensities of the 002 interference and what they termed the amorphous scatter at $2\theta = 18°$, measured from direct x-ray diffractometer tracings. In 1955 and 1956, two reports were published by this laboratory on the evaluation of the crystallinity of cellulose from the x-ray diffraction pictures [1, 2]; the first of our publications is mentioned in the list of references cited in the report [4]. In the two papers from this laboratory, it was suggested that, from measurements of the densitometer curve corresponding to the blackness variations of the Debye-Scherrer x-ray diffraction film of cellulose, there should be derived a ratio which is subtracted from one, and thus there is obtained a figure termed the crystallinity index, CrI. It has been shown that this original CrI can be determined from the main types of cellulose—cotton cellulose, wood cellulose, and regenerated cellulose—as well as from their modifications. Figures 1 and 2 depict how it is suggested that the original CrI be derived from the densitometer curve. The peak nearest to $2\theta = 0$ is known as Peak 1, and the following one Peak 2 (without reference to their relationship to the postulated crystal structures of the cellulose crystal lattices of the different modifications I and II). The height of Peak 2 from the minimum point between Peaks 1 and 2 is measured. This height—called the crystalline height, CrH—is considered as representing the crystallinity of the sample. The distance from the same minimum point to the more or less vertical right-hand side of Peak 2 is also measured. This distance is termed the amorphous width, AmW (see Figures 1 and 2) and is considered as representing the amorphousness of the sample. AmW can easily be expressed as the corresponding $2\theta$ angle, measured in radians. The original CrI can then be calculated as follows:

$$\mathrm{CrI} = 1 - [t \cdot \mathrm{AmW}/\mathrm{CrH}]$$

where $t$ = the full scale deflection of the densitometer-galvanometer when no light is transmitted, measured in mm.; AmW is expressed in radians; and CrH is measured in mm. (cf. [3]).

The original CrI has been put forward as an empirical dimensionless figure which represents the state of crystallinity of cellulose as a whole, and consequently it also depicts the medium cohesion and

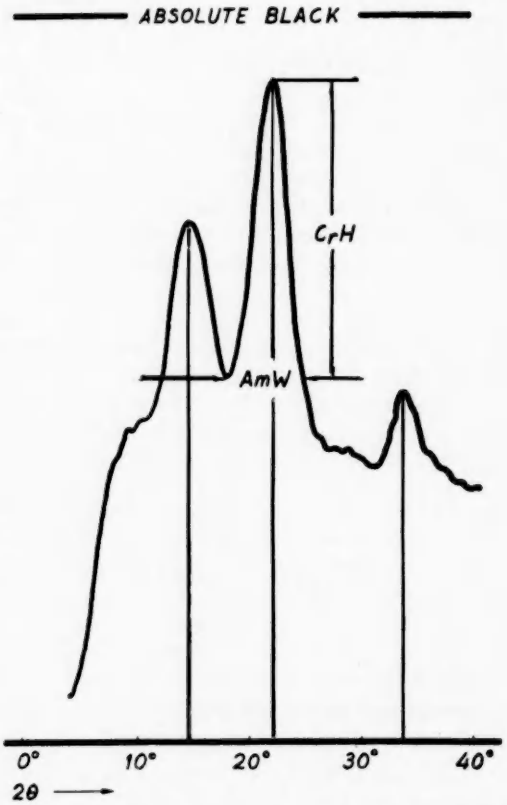


**Fig. 1.** Densitometer curve of x-ray diffractogram of bleached cotton linters.

density of packing of the total macromolecular chain system of cellulose, with no reference to the hypothetical "percentages" of crystalline and amorphous regions. The resistance of cellulose to hydrolytic action of the acid in heterogeneous hydrolysis can also be considered as being a measure of the cohesion and density of packing of the macromolecular chain system of cellulose. In Table I, there is presented a comparison of the original CrI and the corresponding half-life values of native and regenerated cellulose, both untreated and after mercerization in 18% NaOH for 2 hr. at room temperature. It is seen that before mercerization cotton linters have a CrI = 0.73 and a half-life value in 5 $N$ $H_2SO_4$ at 100° C. of 119.4 hr., whereas the corresponding figures for regenerated viscose fiber were found to be CrI = 0.31 and half-life value = 7.4 hr. The mercerization of cotton linters cellulose brings their CrI down to 0.48 and the half-life value down to 45.8 hr. The mercerization of regenerated viscose fiber brings the CrI up to 0.43, and at the same time also the corresponding half-life value up to 36.0 hr. These results support the idea that the original CrI, as well as the hydrolytic half-life values, depend on and depict the cohesion and density of packing of the total macromolecular chain system of cellulose.

**TABLE I**

| | CrI | Hydrolytic half-life, hr, in 5 $N$ $H_2SO_4$ at 100° C. |
|---|---|---|
| Cotton linters | 0.73 | 119.4 |
| Regenerated viscose fiber | 0.31 | 7.4 |
| After mercerization in 18% NaOH at 20° C. | | |
| Cotton linters | 0.48 | 45.8 |
| Regenerated viscose fiber | 0.43 | 35.6 |

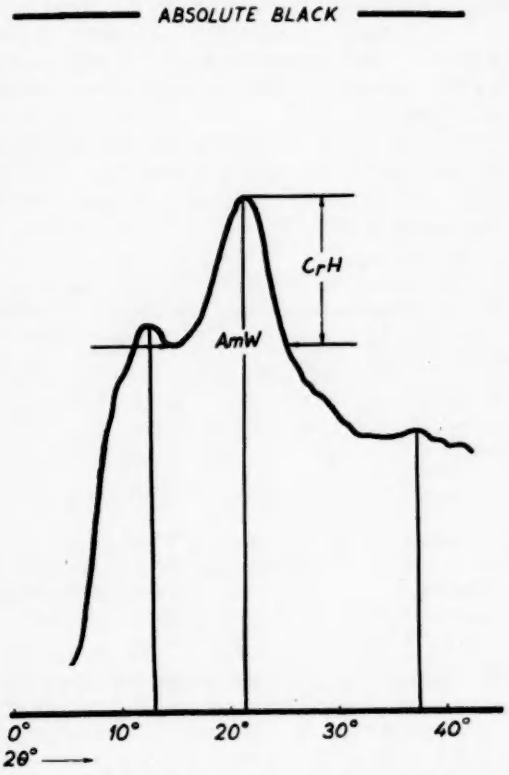


**Fig. 2.** Densitometer curve of x-ray diffractogram of regenerated viscose rayon.

Even if no regard is given to the above views, it must be noted that it leads to general confusion in the field of the x-ray study of cellulose if the same names and abbreviations—in this case Crystallinity Index and CrI—are adapted to mean and to represent things which are completely different. It is therefore hoped that the authors of the first-mentioned paper [4] can hit upon a new name for their relationship in the field of x-ray measurements of cellulose.

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Olli Ant-Wuorinen

# Concerning Terminology for Empirical Measurements of Crystallinity

Southern Regional Research Laboratory[1]
New Orleans 19, Louisiana
January 14, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In his current "Letter to the Editor" Olli Ant-Wuorinen has objected to the use in our recent paper [9] of the term "Crystallinity Index" and of a logical abbreviation of it, namely "CrI." The basis of his objection is that he has already used this same term and its abbreviation in two of his papers [1, 2], one of which we give as a reference in our own paper. He feels that our use of the term and symbol will lead to confusion and proposes that we should "hit upon a new name" for our relationship. He would apparently limit the term "Crystallinity Index" to his "empirical dimensionless figure which represents the state of crystallinity of cellulose as a whole" and which is taken from the height and the base width of the principal (002 in cellulose I; 10$\bar{1}$ + 002 in cellulose II) densitometer peak of a photographic recording of the x-ray pattern of cellulose.

While we regret our unintentional use of the same term and symbol, as used by Dr. Ant-Wuorinen, for our somewhat different set of diffractometer measurements, we do not believe that it is likely to lead to serious confusion. In our opinion this is avoided by the common practice of using authors' names in connection with techniques and procedures. We arrived at the abbreviation, CrI, from Crystallinity Index in the same way that Acid Hydrolysis Crystallinity gave us AHCr and Leveling-Off Degree of Polymerization gave LODP. The word "index" is defined in Webster's unabridged dictionary [11] as "a ratio or other number derived from a series of observations and used as an indicator or measurement of a certain condition." Our usage of the term "crystallinity index," as well as Ant-Wuorinen's, is clearly and logically within the scope of the definition. We do not believe that Dr. Ant-Wuorinen is justified in his claim for exclusive use of the term, either in its entirety or of its components. For example, O'Connor and coworkers [8] use "crystallinity index" in their evaluation of crystallinity of cellulose from infrared spectra. Wakelin and coworkers [10] use "crystalline index" for expressing crystalline content of cottons by an x-ray diffraction technique. Hermans [5] and Clark and Terford [3] have used the term "percent crystallinity" to express their x-ray results, but we feel that this term is too fundamental in its meaning for an empirical method. We do not favor the use of Conrad and Scroggie's "crystallinity number" [4] or Ingersoll's "radial intensity ratio" [6] to express the same relationship derived from x-ray diffraction measurements.

In passing we note that Kouris and coworkers [7] have changed Dr. Ant-Wuorinen's abbreviation "CrI" to "X" to express "percent crystallinity index" instead of using % CrI.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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LEON SEGAL
J. J. CREELY
C. M. CONRAD

# Compressional Behavior of Textile Fibers[1]

Textile Division
Massachusetts Institute of Technology
Department of Mechanical Engineering
Cambridge 39, Massachusetts
December 29, 1959

To the Editor
Textile Research Journal

*Dear Sir:*

Because of its large length/diameter ratio, the textile fiber is most effective in supporting tensile loads. Still, many textile applications do introduce fiber compressions either in a simple form or under complex loading conditions which include bending and tension. The majority of these compressive loadings are directed laterally across the fiber axis. Some usages, however, do involve fiber *axial compression*—despite the early buckling tendencies of unsupported fibrous materials.

Simple bending is a phenomenon calling for tensile and compressive stresses along the fiber axis. The elementary beam theory of elastic isotropic bodies asumes an equal modulus of elasticity in tension and compression in developing a relationship between bending moment, the radius of bending curvature of the neutral axis, and the product of Young's modulus and the sectional moment of inertia. Clearly if the compressive modulus differs from the tensile modulus, the neutral axis will no longer lie at the center of the beam, and the stress distribution will be different on each side of the neutral plane. Thus our knowledge of the bending behavior of fibers must include information as to whether the initial modulus of elasticity is the same in tension as in compression along the fiber axis.

Carrying this thought further, it would be useful to know the stress–strain curve of the fiber in compression, its average modulus to yield, its yield stress, and the slope of the stress–strain curve after yield. What effect does prior compression of the fiber have on its subsequent tensile behavior? Is there a memory effect as in the case of clockwise torsion following counterclockwise torsion? Is there a Bauschinger effect? These questions cannot be dismissed with the claim that buckling precludes the compressive stressing of the fiber. Buckling may accompany compression at an early stage; nevertheless, in compressive buckling, both the *compressive* and *tensile* properties of the fiber determine the ultimate fiber behavior. Futhermore, fibers are often built into dense textile structures where the presence of other fibers provides the lateral support necessary to prevent or at least delay buckling, while compressive stresses are in action. The common household broom and the multipurpose brush provide examples of such support, while another illustration is the close, dense pile of the living room rug. True, the fiber in such materials may eventually buckle under loads of normal usage, but the delay of this buckling under moderate loads is often considered a desirable property in a quality item.

Because of their high strength and flexibility, textile fibers often serve as the reinforcing framework of rubber and plastic structures. In such cases, the matrix in which the fiber is embedded may be subjected to compression and the fiber is prevented from buckling by the solid material surrounding it. This may be observed in light-weight laminated panels used in aircraft construction. The most common instance of the textile–rubber reinforcement, however, is the automobile tire, which is subjected to alternate side wall tensions and compressions with each rotation of the wheel. The coiling of rubber hose (constructed of textile–rubber laminates) furnishes another example of the fiber under compression in circumstances where its tendency to buckle is inhibited by the presence of a surrounding matrix.

Because of its importance in many such end item applications, the compressive behavior of textile fibers have interested several workers in the Textile Division at M.I.T. In some cases, lateral compressive behavior of fibers was the principal subject of their study [2, 4, 5]; in other instances axial compressive behavior was the chief concern [1, 7]. To complement the presentation of John B. Miles in the accompanying letter, we shall restrict this note to a brief report on some of our results in measurement of axial compressive behavior of textile fibers.

The problem of compression testing of fibers pre-

[1] This letter and the one following, by John B. Miles, represent independent exploratory studies of fiber axial compressional behavior. The authors have exchanged and reviewed each other's communications, and conclude the material of each confirms and/or supplements the other; they have requested that the letters be published simultaneously. —*Editor.*

sents many more problems than are encountered in ordinary compression tests on large specimens. First, of course, is the matter of preparing the specimen of sufficiently small height as to insure true compression, to the exclusion of buckling. Second is the matter of applying loads or strains at a known rate to permit reproducibility of results on the visco-elastic textile fiber. Third is the difficulty of measuring the small strains or loads involved in compression of single fibers. Fourth is the effect of end restraint on the compression behavior of the fiber.

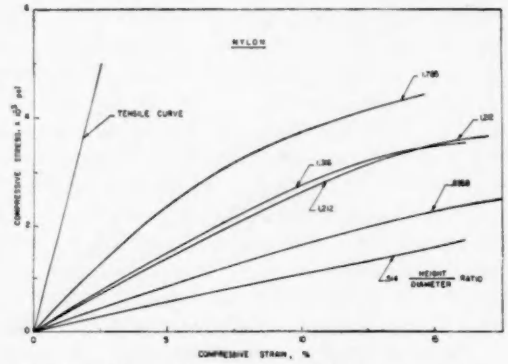


**Fig. 1.** Compressive stress–strain behavior of nylon.

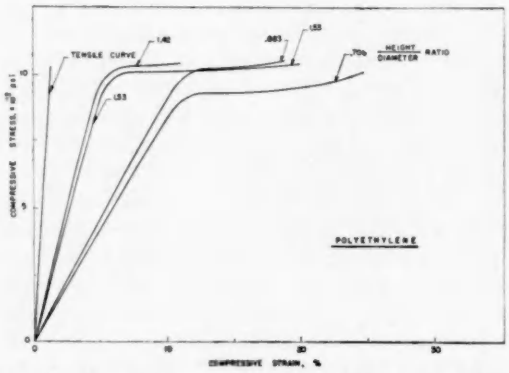


**Fig. 2.** Compressive stress–strain behavior of polyethylene.

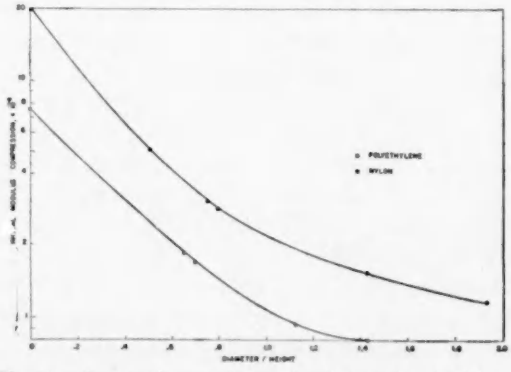


**Fig. 3.** Compressive modulus of nylon and polyethylene.

The metal technologist and mechanical engineer have eliminated the problem of end restraint by lubricating the top and bottom of the cylinder of metal before initiating the test and relubricating the specimen after small increments of strain. We have not attempted to lubricate our specimen for three reasons: (1) the unknown effect of the lubricant on the fiber, (2) the difficulty of handling a small fiber specimen is great enough without adding to its elusiveness through lubrication, (3) the effect of the squeezing out of the lubrication layer on the recorded strains. Without lubrication, some end effect may be expected. For information on the nature of this effect, we refer to the work of the metal technologists.

A concise summary of the early studies in compression testing appears in Nadai's book [6], in which it is pointed out that when a metal cylinder is compressed, the material directly adjacent to the compression jaws is prevented from spreading laterally by friction. This effect penetrates into the specimen and forms two conical zones (in hourglass fashion) which are deformed less than the remaining material of the cylinder. The resistance of these zones to further deformation is greater than that of the remaining material. In tall cylinders (large height:diameter ratio) the effect of the semirigid conical zones is less, relative to the mass of the material, than in short cylinders. This suggests the testing of cylinders of varying heights with a view to getting a range of compressional resistances for each percent reduction of height of the specimen [3]. The resistances for each compressive strain may then be plotted against the diameter:height ratio and extrapolated back to zero diameter:height ratio, i.e., to the case of the cylinder of such great length that its end effect is negligible. In practice, of course, such a cylinder would buckle before yielding in compression. If one then replots the extrapolated resistance for each percent reduction in height against that reduction, a true stress–strain curve should result. We have followed this "variably dimensioned specimen" technique in our axial compression tests of textile fibers.

For axial fiber compression, we have built a

single lever chainomatic loading device. The loading rate of our first instrument was set at 44 g./min., and compressive deformations were measured by means of a traveling microscope. Later versions of the instrument allowed for controlled variation of the loading rate, provided compressive strain measurement by means of a differential transformer type strain gauge, permitted tests under wet as well as under dry conditions, and allowed for simultaneous vertical viewing of the specimen during the compression test (of use in determining contact areas between fiber and the compressive plane).

The specimens were prepared from straight monofilaments by lateral cutting with a new razor blade at random lengths in the range of height:diameter ratios of 0.4 to 2.0. The cut specimens were graded as to length, and only those segments with square ends were retained. Numerous cuts were required to prepare one suitable specimen, and even then the effect of the end geometry could not be certain until the actual compression test had been completed and the conduct of the specimen observed. The results of numerous tests were vitiated by a buckling of the specimen at an early stage in the experiment.

The materials tested in the compression device were polyethylene monofilament (50 mils diameter), nylon monofilament (9 mils), and saran monofilament (10 mils). The axial compressive stress–strain curves of the polyethylene and nylon monofilaments are presented in Figures 1 and 2 respectively, for a range of height:diameter ratio specimens. The initial portion of the tensile curve for the same material monofilament is plotted in each figure. In Figure 3 the initial modulus derived from each compressive stress–strain curve is plotted against diameter:height ratios for both polyethylene and nylon specimens. The nylon and polyethylene materials used in this study are not representative of any particular commercial product.

It is clear in the stress–strain curves plotted for both nylon and polyethylene monofilament that the initial modulus is strongly influenced by the height:diameter ratio of the specimen. This suggests the importance of the "end" restraint. But such an effect should be evidenced in the appearance of excessive specimen barrelling during compression tests. This was not observed.

In the nylon tests, the value at which the compressive stress appeared to level off varied with specimen dimensions. In the polyethylene tests, the "yield" stress in compression appeared to be independent of specimen geometry. In both cases, the yield stress in compression fell far below the apparent yield in tension.

The strong dependence of initial modulus on specimen geometry suggested the presentation of Figure 3, in which the initial modulus in compression is plotted against the diameter:height ratios of both nylon and polyethylene. Extrapolation of the inital compressive modulus to the case of the infinitely long specimen ($D/H = 0$) provided moduli of 200,000 psi for the nylon and 75,000 psi for the polyethylene. These extrapolated compressive values were in close agreement with the tensile moduli measured for the same material.

It would appear that there were no end "hard" zones in those axial tests of fiber compression. Had such zones existed, the short stubby specimens would have demonstrated stiffer rather than softer compressive behavior than their long slender cousins. At this time, one can only postulate the presence of excessive end stresses due to sample cutting. The presence of such damage would cause more of a "softening" effect on the relatively short specimen.

Clearly the field of axial compression testing of fibers warrants some of the attention given thus far to tensile behavior of textile products.

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STANLEY BACKER

# Compressional Behavior of Textile Fibers[1]

Chemstrand Research Center
Decatur, Alabama
November 30, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

Most discussions of the bending of fibers have followed the principles of elementary elastic theory, assuming that the moduli in tension and compression are equal and that there is an unstrained neutral plane in the center of the section. Even for small strains, the tensile stress–strain curve of nylon is not linear, and there is no published information about the stress–strain behavior in compression in the direction of the fiber axis. Stimulated by these considerations, we have made direct measurements in essentially uniaxial compression on an oriented nylon 66 bristle which had sufficiently large dimensions to make the preparation of cylindrical samples and the measurement of deformation possible.

A progress report on measurements made by this method was given at the Spring 1959 meeting of The Fiber Society, Inc., at which time it was brought to our attention by Stanley Backer that he had made similar measurements which he described at the 1957 Gordon Conference but had not published. We agreed that it would be desirable for each of us to give a brief description of this work in letters to TEXTILE RESEARCH JOURNAL.

The 66 nylon bristle used in our work was a commercial type about 1.5 mm. in diameter. The x-ray diffraction pattern and double refraction measurements on a wedge section corresponded to an effective draw ratio of 4 to 5. The samples for compression measurements were made in the following manner. Holes were drilled in a $\frac{1}{8}$-in. thick steel plate of a diameter to give a tight fit when the bristle was inserted in it. Several of these holes were drilled in the plate, bristle samples were inserted and roughly trimmed off at the surface of the plate, and then the two surfaces of the plate and bristle were carefully ground. The small bristle cylinders were then pushed out from the plate. The cylinder height depended on the amount of grinding, and for most of the measurements to be described ranged from about 2.2 to 2.7 mm. The ratio of cylinder height to diameter was slightly less than 2. A slight curvature in the bristle as supplied was substantially eliminated by suspending a 1-kg. load from a length of the bristle (about 0.05 g./den.) in boiling water for $\frac{1}{2}$ hr.

The compression measurements were made on the Instron using a compression load cell. The bearing surfaces were lubricated in order to obtain as nearly as possible uniaxial compressive stress. The effectiveness of the lubrication was judged by pressing samples to well beyond the elastic limit and examining the curvature of the side surfaces or barrel shape, indicating some slight restraint at the bearing surface. There was no evidence of buckling. Of the several materials tried, tricresyl phosphate appeared

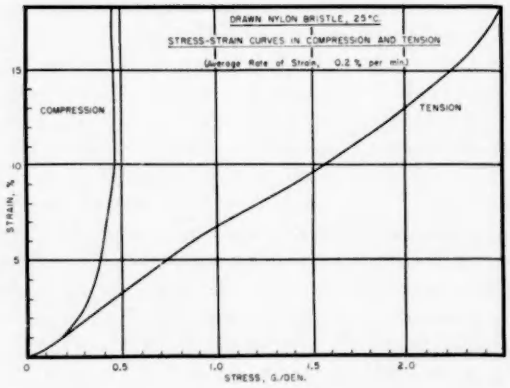


**Fig. 1.** Stress–strain curves of oriented nylon bristle in tension and compression.

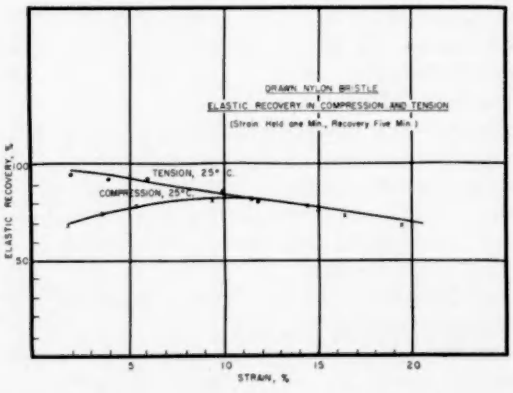


**Fig. 2.** Elastic recovery of oriented nylon bristle in tension and compression.

[1] Contribution No. 62 of the Chemstrand Research Center.

to be as effective as any and was used for most of the measurements. The compression strains were imposed in a step-wise manner on the Instron and the amount of compression was determined by a sensitive dial gauge measuring the separation of the bearing surfaces and eliminating the deflection of the load-measuring cell.

Figure 1 gives a comparison of the stress–strain curves for compression and tension at room temperature, both types of strain being carried out in a step-wise manner of approximately 1% strain held for 5 min.; the load at the end of that time was then taken. Above about 1% strain the curves are strikingly different. The accuracy of measurement was not sufficient to determine whether the curves are identical below this point. At 2% strain, the stress in compression is about 15% less than that in tension. The tension curve has the familiar slight curvature toward the load axis, whereas the compression curve bends markedly toward the strain axis. The stress in compression reaches a maximum of about 0.45 g./den., after which it actually falls off. The stress–strain curve in compression is quite similar to that of undrawn nylon in tension.

The appearance of the curve in the region of 10% strain and above at first glance would seem to indicate that a process similar to the reverse of drawing was taking place and that the elastic recovery and stress relaxation behavior at strains above 10% would be quite different from those in tension. However, it was found that the elastic recovery behavior was quite similar up to strains as high as 20%. A measure of the elastic recovery was obtained by applying a strain at a rate of 20%/min., holding that strain for 1 min., reducing the strain until the load fell to zero at the same rate, and allowing the sample to recover under zero load for 5 min. The same sample was used throughout the test, being given successively greater strains after each recovery. In Figure 2 a comparison is shown of the recovery in tension and compression at successive strains up to 20%, in which the percent of the strain imposed at each step and recovered at the end of the period is plotted against the strain. Under these particular conditions, the recovery in compression was less than in tension up to about 10% strain and from then on the two were equivalent.

The tensile and compressive behaviors were also compared in stress relaxation experiments which will not be described here.

The effect of temperature has been explored in a preliminary way using electrically heated plates. At 100° C. the stress–strain curve in compression was similar in shape to that at 25° C. up to about 6% strain with the stress about 0.45 that at 25° C. The stress reached a maximum at 6% strain of only 0.18 g./den. The elastic recovery at 100° C. was very different from that at 25° C., strains above 5% being nonrecoverable.

The striking differences between the tensile and compressive behavior of oriented nylon indicate that the bending behavior of oriented fibers in general may not be predictable from measurements of the tensile behavior alone.

JOHN B. MILES

# Book Review

**Hydrogen Bonding.** Edited by D. Hadži with the cooperation of H. W. Thompson. New York, Pergamon Press, 1959. xii + 571 pages. Price $17.50.

*Reviewed by Walter Lobunez, Textile Research Institute, Princeton, N. J.*

This book contains the papers presented at the Symposium on Hydrogen Bonding held at Ljubljana, Yugoslavia 29 July–3 August 1957 under the auspices of I.U.P.A.C. Important discussions at the symposium regarding the definitions and the nature of the hydrogen bond are also included.

Scientists from 17 countries participated at these meetings, and the reader can find in this book new theoretical considerations and results of experimental work accomplished by the leading experts of the world.

There are 58 papers listed in the contents (5 of them were submitted in condensed form). An asterisk denotes introductory papers (9 of the 10 were submitted in full length). They present a description of various experimental approaches and of theoretical treatments that are used for studying the subject of hydrogen bonding.

The first introductory paper, by Linus Pauling, is

"The Structure of Water." A structural model based on a particular configuration involving labile complexes of 21 water molecules, 20 of which lie at the corners of a pentagonal dodecahedron (each of them forming three H-bonds with the adjacent neighbors in the dodecahedron) and the 21st forming no hydrogen bonds and occupying the central position in the dodecahedron, is proposed.

This model seems to account in a reasonably satisfactory way for several properties of water, including the dispersion of dielectric constant and the radial distribution curve as determined by x-ray diffraction.

The second introductory paper, by J. D. Bernal, is concerned with the place the hydrogen bond plays in known structures, largely with the known extended structures of crystalline solids and liquids. The special case of hydrogen bonds in polymeric structures such as cellulose, proteins, and nucleic acids is also discussed here.

Next of the introductory papers is by G. E. Bacon and deals with the study of H-bonds by neutron diffraction. One cannot but agree with the author that the use of neutrons offers the most powerful means for accurately locating the positions of the hydrogen atoms. Examples of Fourier projections of the atomic nuclei in hydrogen bonded crystals based on the measurements of the intensity of neutron scattering by single crystals are illustrated in several figures included in this paper.

The type of information which can be derived from proton resonance measurements, the advantages and limitations of the method, and how it compares with results obtained by other methods are discussed in the paper of W. G. Schneider, "Proton Magnetic Resonance Measurements of Hydrogen Bonding."

N. Sheppard's paper deals with infrared spectroscopy and hydrogen bonding, especially with changes in band width and with frequency shifts caused by H-bonding. A list of 65 references follows this paper.

Ernst Lippert reviews in 40 pages the results of some works on electronic and fluorescence spectra and shows that the present knowledge about the nature of H-bonds and the consideration of the electronic structure of participating molecules aid in explaining results. Fifty-six references are listed at the end of this paper.

In "Dispersion Dielectric et Liaison Hydrogene" by M. Magat the author discusses the information that can be obtained by this method about motion of molecules in a liquid, duration of existence and the rate with which complexes of molecules connected by H-bonds re-form, and the mean number of molecules in these complexes and its change with temperature. This latter variation permits one to calculate the dissociation energy of the H-bond. Experimental results for alcohols are given and discussed.

"The Hydrogen Bond" by C. A. Coulson opens the series of theoretical contributions at this symposium. A review of the concepts used in theoretical interpretation of the H-bond is given. The nature of the potential energy function which describes the motion of part or the whole of the bonded region is considered, and several lines of work which appear to the author worth following are suggested. A most interesting discussion follows this paper.

The last paper of introductory character, "The Hydrogen Bond Energies" by Mansel Davies, contains a review of some of the more significant methods of determining H-bond energies. The significance of the gas-phase values is emphasized for the reason that they alone are relevant in a precise comparison with theoretical estimates. Solution values and their dependence upon the medium, and some studies on H-bond energies for substances in solid state, are discussed.

Many papers that do not belong to the group of introductory papers, being of a more specialized nature, are still of great importance.

Some investigators used other methods besides those covered in introductory articles. For instance, Wilhelm Maier studied ultrasound absorption for determination of the rates of association and dissociation of the H-bonded complexes.

The influence of H-bonding on various physicochemical systems, on properties of individual and of aggregates of molecules, is discussed in many papers.

It must be mentioned here that several papers in this book are in German and several in French, but most are in English.

"Hydrogen Bonding" can be of immense value to a beginner in this field, as well as to one who spent many years working on this subject. Since the properties of many natural and synthetic fibers depend on the presence of hydrogen bonds, this book would be an advisable acquisition to a textile chemist's library.

# INTERNATIONAL SEARCH

Opportunities for Physicists—Physical Chemists—Fiber Scientists

## FIBER CHARACTERIZATION RESEARCH

The planned expansion of the programs and staff of the Chemstrand Research Center, Inc., involve establishment of a Fiber Characterization Section to:

Characterize experimental fiber forming materials, relating their properties back to their molecular structure and forward to end product performance

Develop fiber evaluation techniques and instruments

Perform physical analysis associated with fiber, yarn and end product evaluation.

Challenging assignments are available at several levels of responsibility including direction of the Section's activities. Academic training in Physics, Physical or Polymer Chemistry, or Fiber Mechanics and considerable experience in the above areas of the textile fiber and related fields are prerequisite for the individual selected to head this program. Demonstrated ability to organize and administer broad theoretical and applied research studies also required. Similar training and interests but less experience needed for other interesting opportunities in this group. The importance and complexity of this fundamental investigational work will be recognized in commensurate salaries and professional climate.

The Chemstrand Research Center, Inc.—a wholly owned subsidiary of the young and vigorous Chemstrand Corporation—will relocate in late 1960 from its present Decatur, Alabama site to new laboratories in the Research Triangle area of North Carolina.

European interviews can be arranged for applicants who are noncitizens of the United States and have decided to immigrate to this country.

If you are interested in associating with these new programs of an expanding research organization, contact or send resume of academic background and experience in strictest confidence to:

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